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Evaluation of Hazardous Waste Incineration in Cement Kilns at San Juan Cement Company

Monsanto Research Corp., Dayton, OH

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EVALUATION OF HAZARDOUS WASTE INCINERATION IN CEMENT KILNS AT SAN JUAN CEMENT COMPANY

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Contract No. 68-03-3025

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16. ABSTRACT

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The destruction and removal efficiencies (DRE) of the POHC's ranged from 91.043 percent to 99.997 percent, with only 6 percent of the DRE's greater than 99.99 percent. Poor DRE results were attributed to the absence of waste atomization and the difficult incinerability of chlorinated monocarbon compounds. It was found that about 82 percent of the input chlorine appeared in the cement clinker. The amount of chlorine appearing in the baghouse dust varied from 5 percent to 26 percent of total chlorine input. The total absorption of the HCl formed averaged 99.7 percent in seven tests. PCDD's and PCDF's were not produced at detectable levels when the cement plant was operating normally.

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FOREWORD

When energy and marterial resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes a demonstration program on hazardous waste incineration in a wet process Portland Cement Kiln. It will be used to support technically defensible regulations in the evaluation of the future effort to develop the technology. The regulatory agencies as well as cement plants contemplating the use of waste fuels will find the results presented in this report helpful.

Requests for further information regarding the incineration of hazardous wastes in cement kilns should be directed to the Chief, Incineration Research Group, Energy Pollution Control Division, IERL, Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Cement kiln incineration of chlorinated liquid organic wastes was investigated in a 5-month demonstration program at San Juan Cement Company in Puerto Rico. Chlorinated monocarbon compounds (POHC's) were monitored in the waste and emissions, and the fate of added chlorine in cement production was determined. Seven levels of percent chlorine in the waste were burned at ten different waste feed rates. Extensive sampling and analysis was conducted to look for the potential presence of polychlorinated dibenzodioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's).

The demonstration and removal efficiencies (DRE) of the POHC's ranged from 91.043% to 99.997%, with only 6% of the DRE's greater than 99.99%. Poor DRE results were attributed to the absence of waste atomization and the difficult incinerability of chlorinated monocarbon compounds. It was found that about 82% of the input chlorine appeared in the cement clinker. The amount of chlorine appearing in the baghouse dust varied from 5% to 26% of total chlorine input. The total absorption of the HCl formed averaged 99.7% in seven tests. PCDD's and PCDF's were not produced at detectable levels when the cement plant was operating normally.

This report was submitted in fulfillment of Contract 68-03-3025 by Monsanto Research Corporation under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from August, 1981 to March, 1982, and work was completed as of August, 1983.

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SECTION 1

INTRODUCTION

Some attractive alternatives to hazardous waste incineration which make use of a waste's heat content are cofiring of hazardous wastes in high temperature industrial processes. Many such processes, which include cement and dolomite kilns, glass furnaces, steel furnaces, and some industrial boilers, provide conditions of temperature and residence time similar to those required for dedicated hazardous waste incinerators. In addition to the savings derived from the heat value, the use of existing industrial processes requires less capital to process a given amount of hazardous waste.

In particular, cement kilns, because of large process capacities and energy use, appeared to be an excellent example of this concept. They typically operate at temperatures over 1,260°C (2,300°F), gas residence times are in excess of 1.5 seconds at or above this temperature, and the combustion zone is highly turbulent.

The alkaline environment in a cement kiln absorbs acid gases such as HCl, eliminating the need for additional special gas scrubbing systems. Incineration of chlorinated wastes generates hydrogen chloride, and recovery of HCl is usually done by combustion gas scrubbing, thereby generating a liquid waste requiring disposal.

A number of cement plants have been used to test cofiring of hazardous wastes, eg., St. Lawrence Cement Company in Mississauga, Ontario in 1974-1976; Peerless Cement Company in Detroit, Michigan, in 1976; Stora Vika Cement Plant near Stockholm, Sweden, in 1978; and Marquette Cement in Oglesby, Illinois, in 1981. Although the data from these tests indicated that cement kilns, when properly operated, could destroy most organic chemical wastes, a need remained within EPA for criteria to use in evaluating permit requests from cement plants to burn wastes, particularly those which are highly chlorinated hydrocarbons.

Because of the need to gather more data on the effects of burning waste on emissions from the cement process, the Industrial Environmental Research Laboratory-Cincinnati conducted a comprehensive demonstration program at San Juan Cement in Dorado, Puerto Rico, from October 1981 until February 1982. The purpose of the demonstration program was to generate permit evaluation criteria for the EPA, demonstrate that hazardous chlorinated chemical wastes can safely and effectively be used as supplemental fuel in wet process cement kilns duing the production of portland cement, and recommend techniques for the proper management of waste fuel programs at industrial kiln plants.

A sampling and analytical program was conducted during the burning of the hazardous waste. The primary goal of the sampling and analytical program was to evaluate the effects of various waste parameters on the destruction efficiency of Principal Organic Hazardous Components (POHC's), and change in emissions of particulate matter, hydrocarbons, CO, SO_2, NO_x, and HCl. Secondary objectives were to detect and quantify the Products of Incomplete Combustion (PIC's), chlorinated dibenzofurans, chlorinated dibenzodioxins, trace metals and heavy organics.

The facility at San Juan Cement Company was chosen for the test due to its availability, the willingness of the company to cooperate with the Puerto Rican Environmental Quality Board (PRJCA) and U.S. EPA Region II in obtaining permits, and the suitability of the facilities for a test.

Both San Juan Cement and the PRJCA are interested in pursuing the technology for fuel cost-reductions and environmental control cost-reduction aspects, respectively. Presently, San Juan Cement burns imported No. 6 fuel oil, which can account for up to 65% of the cost of producing cement clinker. Use of the waste to reduce fuel costs could have a marked positive impact on plant profitability because waste disposal costs in Puerto Rico are very high (up to $7.00 per gallon of waste). The use of cement kilns as an incineration option in Puerto Rico would reduce costs for waste generators, providing an incentive for ultimate disposal on the island rather than mainland U.S. or ocean disposal.

The following sections describe the site and facilities in detail, and the results of the sampling and analysis program.

SECTION 2

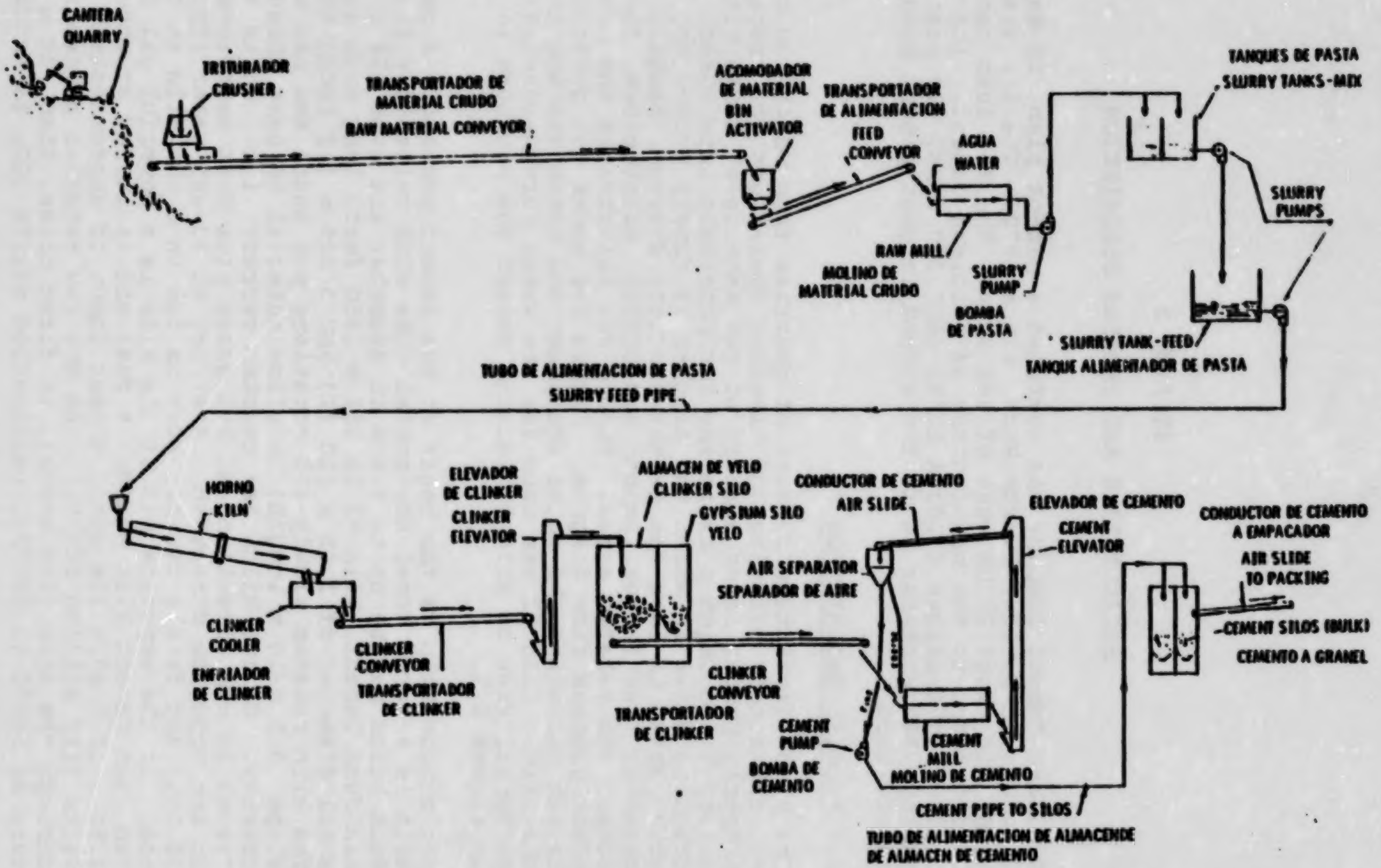
PROJECT SITE AND PROCESS DESCRIPTION

San Juan Cement Company has operated a cement plant in Barrio Espinosa in Dorado, Puerto Rico, since 1970. The location of the plant, is about 27 km west of San Juan. The San Juan cement plant is dedicated to the manufacture of portland cement. Its annual production averages 4.082 x 10^8kg (450,000 tons) per year and it employs 350 workers; it is the second largest cement plant in Puerto Rico.

2.1 PROCESS DESCRIPTION

The plant facilities consist of quarries from which raw materials are extracted; grinding and blending operations for preparing a properly proportioned mixture of raw materials; three wet-process rotary kilns which convert the raw materials into cement clinker; grinding mills in which the clinker is finely ground and mixed with gypsum to form the cement product; storage, bagging, and material transfer equipment; and office, maintenance, dust disposal, and related areas. Figure 2-1 illustrates the cement plant process flow diagram. Figure 2-2 shows the general plant layout including the major equipment and waste storage area at the site. Kiln #2 was used for the waste burn demonstration. A pictorial view of kiln #2 looking toward the baghouse is given in Figure 2-3.

The cement kiln is the heart of the cement process. A cement kiln is a large steel horizontal tube with refractory linings. Such kilns may be up to 7.6 m in diameter and over 232 m long; at San Juan Cement, kiln #2 is 137 m (450 feet) long with an outer shell diameter of 3.05 m (10 ft) and 0.305 m (12 inch) thick walls. The kiln rotates slowly (75 rotations per hour) and has a gentle slope (0.3 m/10 m length) to allow material to pass through by gravity. Cement kilns are counter current; i.e., solid materials travel in one direction and hot gases plus dust emissions travel in the opposite direction. A slurry of 30-40% water (typically 35-39%) and finely crushed rock is fed into the kiln at the upper end. At the opposite end of the kiln is a powerful oil fire; at San Juan Cement kiln #2, No. 6 fuel oil is burned at about 1.51 x 10^{-3} m^3/s (24 gpm), a heat input of approximately 62 x 10^6 watts (212 million Btu/hr). As the raw material passes slowly through the kiln (1-4 hours), it first dries, then, at a temperature of 550°C (1,020°F), calcination starts (CO_2 is extracted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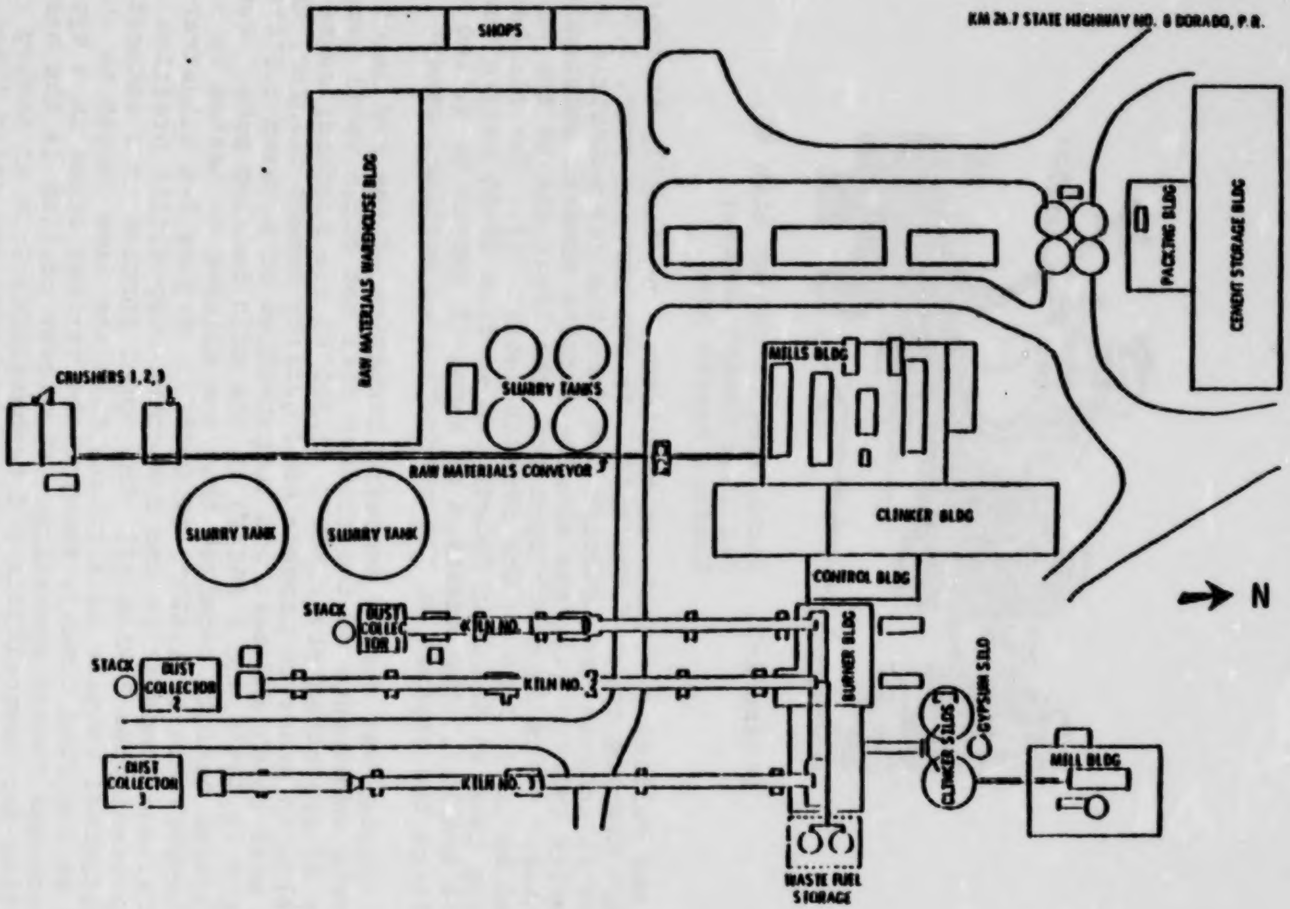
CONDUCTOR DE CEMENTO
AIR SLIDE
AIR SEPARATOR
SEPARADOR DE AIRE
CEMENT
PUMP
BOMBA DE
CEMENTO
CEMENT
MILL
MOLINO DE CEMENTO
ELEVADOR DE CEMENTO
CEMENT
ELEVATOR
CEMENT PIPE TO SILOS
TUBO DE ALIMENTACION DE ALMACENDE
DE ALMACEN DE CEMENTO
CONDUCTOR DE CEMENTO
A EMPACADOR
AIR SLIDE
TO PACKING
CEMENT SILOS (BULK)
CEMENTO A GRANEL

Figure 2-1. Cement plant flow diagram.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CONTROL BLDG
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BURNER BLDG
GYPSUM SILO
CLINKER SILOS
MILL BLDG
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KILN NO. 3
WASTE FUEL STORAGE

Figure 2-2. San Juan Cement Company plant layout with waste fuel storage site.

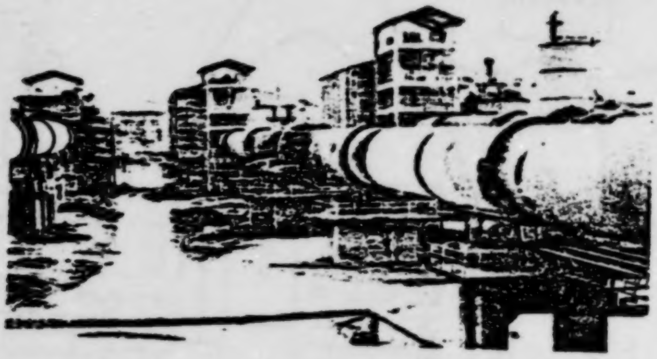

Figure 2-3. South view of cement kiln #2, San Juan Cement Company, Dorado, Puerto Rico.

from the calcium carbonate in the feed), and finally it approaches the hot burning zone of the kiln. In the burning zone, 1,500°C (2,700°F) temperatures calcine and fuse the raw materials creating a complex calcium silicate alumino-ferrite mineral substance called "clinker," which is discharged from the lower end of the kiln and cooled by large fans in the clinker cooler [1]. The clinker production rate at San Juan Cement ranged from 28-33 metric tons/hr (31-36 ton/hr). The addition of about 6% gypsum to milled clinker completes the process in the production of portland cement.

In a typical wet cement process, formation of the key calcium silicate components of the clinker does not begin until temperatures of approximately 1,260°C (2,300°F) are reached; consequently, in order to produce good quality cement clinker, the kiln must reach and maintain temperatures of between 1,370°C - 1,450°C (2,500°F and 2,650°F) in the kiln burning zone. Control of clinker quality requires that the clinker be heated to a minimum temperature of 1,427°C (2,600°F). Figure 2-4 illustrates the generalized temperature and component composition profiles in a wet-process cement kiln [2]. The upper portion is a schematic longitudinal section of a rotary kiln the same length as the kiln used at San Juan Cement, showing the various zones in a typical wet-process cement operation. The lower portion is the base-run solution for compositions and temperatures from an analog computer. The broken lines are temperature profiles; the solid lines represent mass distribution.

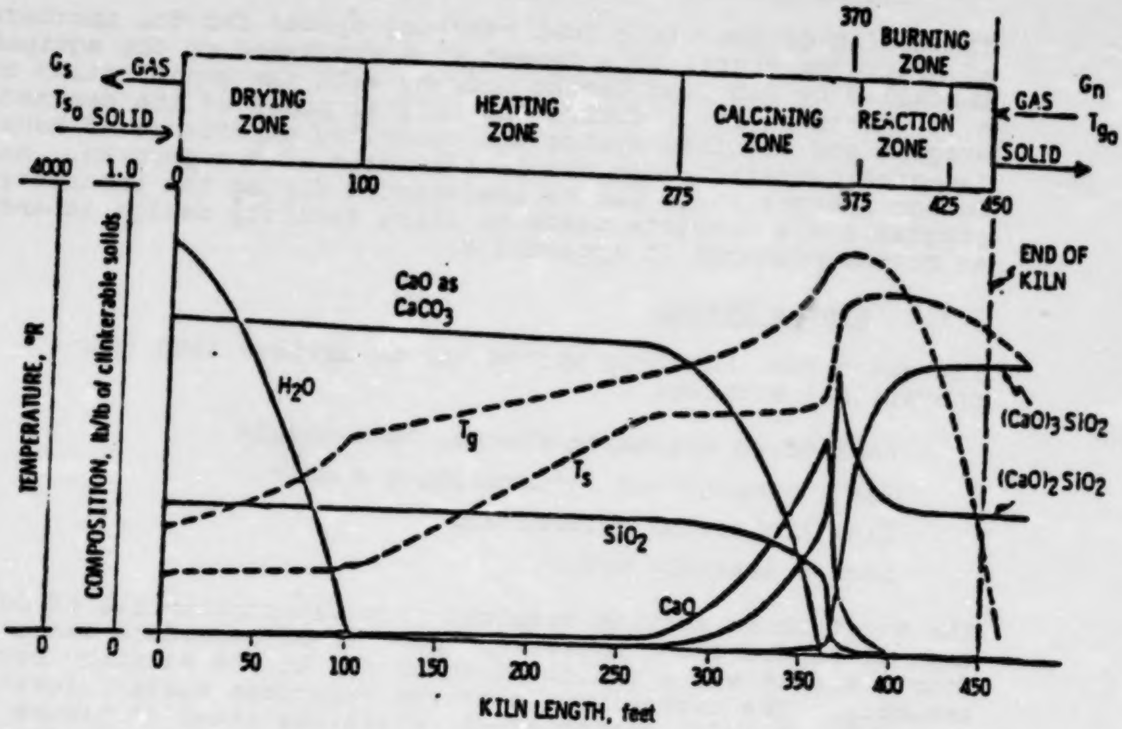

Figure 2-4. A profile of temperature and composition of components of a wet-process rotary cement kiln [2].

The wet-process kiln combines drying, calcining, and reaction in a single unit, and thus is perhaps the most complex of all rotary-fired equipment. The kiln gas temperature, T_g rises rapidly at the firing end of the kiln (right side in Figure), then falls smoothly to an exit temperature of around 230°C. The temperature of the solid material, T_s, remains low until the H_2O is driven off, then rises through the heating zone, levels off through the calcining zone, and rises abruptly at the reaction zone. Its overall profile remains slightly cooler than the gas temperature, reflecting the time lag of heat transfer from gas to solid.

Exhaust gases from kiln #2 pass through a baghouse type dust collector where entrained particulate matter is removed. The cleaned exhaust gases are then released to the atmosphere through a single stack. The baghouse employed at kiln #2 consists of 1,536 fabric filters, each 9.3 m in length. The efficiency of the baghouse in removing particulate matter from the gas stream is reported to be 99.8 percent [3]. It was not an objective of this program to determine the baghouse collection efficiency.

2.2 WASTE FUEL HANDLING SYSTEM

The design of the waste fuel handling system for the incineration of hazardous wastes in a cement kiln was based on the equipment installed by San Juan Cement Company with the consultation of A. T. Kearney, Inc., during the initial phase of the demonstration program and modified during the operating experience of Monsanto Research Corporation in the latter phase of the program. Many design changes could not be implemented during the demonstration program and a complete waste handling facility design is included as recommendations in Appendix B.

2.2.1 System Design

The waste fuel handling system can be divided into four operational modules:

- tank truck unloading storage tank module
- waste pumping and recirculation module
- flow monitoring module, and
- burner assembly module.

The first three modules required particular materials of construction to handle the corrosive properties of hazardous wastes. The fourth module was a modification of the kiln's existing burner assembly. The corrosiveness of the hazardous wastes dictated the use of black iron, carbon steel, stainless steel or bronze (in order of preference). Brass and galvanized steel were found to be totally unacceptable.

2.2.2 Tank Truck Unloading and Waste Storage Module

Waste arrived at the plant in RCRA-approved truck tankers which hold 37.85 - 47.32 m^3 (10,000 to 12,500 gallons). Figure 2-5 depicts the flow system for this module. A 7.6 cm (three-inch) hose with quick-connections was used to transfer liquid from the tank truck; a 5.1 cm (two-inch) hose was used as a vapor return line from the storage tanks to tank truck. A stainless steel strainer with a sieve size of 1.6 mm (1/16 inch) prevented solids from getting into the unloading pump, which was an Ingersoll-Rand type H-HC centrifugal pump rated at 1.26×10^{-2} m^3/s at a head of 9.1 m (200 gpm at a head of 30 feet). The piping and valving system was arranged so that the tanks could be unloaded to a truck; i.e., operated in reverse. Two 37.85 m^3 (10,000-gallon) vertical, flat-bottom carbon steel storage tanks placed on a concrete pad were used to hold waste until it was burned. Liquid level was measured by a pressure gauge installed at the bottom of the tank side with readout in "feet of head." Storage tank vapors were vented to two drum-sized granular activated carbon adsorbers in series to control storage tank "breathing" emissions. Storage tank vapors were returned to the tank truck during unloading.

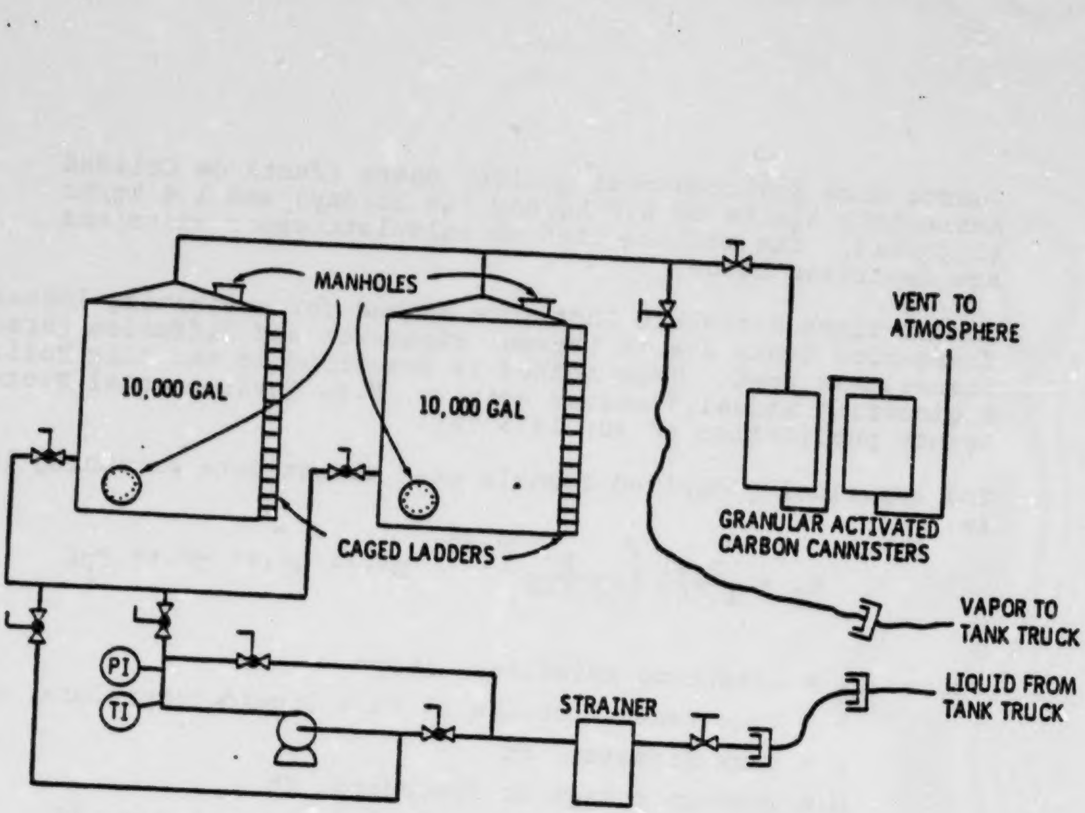
MANHOLES
10,000 GAL
10,000 GAL
CAGED LADDERS
VENT TO ATMOSPHERE
GRANULAR ACTIVATED CARBON CANNISTERS
VAPOR TO TANK TRUCK
LIQUID FROM TANK TRUCK
STRAINER
PI
TI

Figure 2-5. Tank truck unloading and waste storage module.

The concrete slab supporting the storage tanks and unloading pump was surrounded by a sealed steel retaining wall (dike) so that any spill at the storage facility could be completely contained.

Acceptable engineering design criteria for dikes surrounding bulk storage dictate that 1) dike materials be designed to be chemically resistant and essentially impervious (e.g., permeability rate no greater than 10^{-7} cm/s when subjected to a head of 0.305 m of water), and 2) the capacity of the dike area be at least adequate to hold the entire tank contents plus a reasonable allowance for precipitation, typically 0.305 m of freeboard [4]. The steel retaining wall with silicon sealing met the permeability design criterion, and the waste fuel tank dike holding volume was:

$$7.315 \text{ m} \times 10.973 \text{ m} \times 0.991 \text{ m} = 79.545 \text{ m}^3 \qquad (1)$$

which was sufficient to contain a catastrophic failure of both tanks.

The waste fuel loading and storage module was designed to minimize vapor emissions from the organic liquids stored and burned at San Juan Cement. It was estimated that total organic vapor emissions were less than 0.91 kg/day (2 lb/day). This is well below the

Puerto Rico Environmental Quality Board (Junta de Calidad Ambiental) limits of 6.8 kg/day (15 lb/day) and 1.4 kg/hr (3 lb/hr). The methods used to calculate vapor emissions are described below.

The American Petroleum Institute method for estimating losses from fixed-roof tanks due to thermal expansion and diffusion (breathing losses) was used. This method is described in the "Air Pollution Engineering Manual," second edition, U.S. Environmental Protection Agency publication AP-40, 1973 [5].

The empirically derived formula used to estimate breathing losses is:

$$L_B = \frac{2.21}{1,000}\left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_pC \qquad (2)$$

where L_B = breathing emissions, lb/yr

P = true vapor pressure at bulk liquid temprature, psia

D = tank diameter, ft

H = average outage or freeboard, ft

T = average daily ambient temperature change, °F

F_p = paint factor

C = adjustment factor for small-diameter tanks

The way in which each factor in equation (2) was determined is as follows:

P, vapor pressure, was calculated for a mixture of organic liquids with a composition equal to that of the most volatile fuel expected to be used in the demonstration. Table 2-1 lists the substances in this "worst case" fuel and their corresponding concentrations and pressures in the fuel and vapor. All pressures were selected at the average ambient temperature at San Juan International Airport, 26°C or 78.6°F.

D, the tank diameter, is 10.5 feet.

H, the average tank outage, represents the space above the liquid surface in the storage tank. Maximum emissions would occur when the tank is nearly empty and H = 16.5 feet, the height of the tank.

T, the average ambient temperature change, as recorded at San Juan Airport, is the difference between the average ambient low temperature (72.0°F) and the average ambient high temperature (85.2°F) or 13.2°F.

TABLE 2-1. FUEL CONCENTRATIONS AND VAPOR PRESSURES[a]

Compound	Weight, %	Molecular weight	Mole fraction	Pure vapor pressure	Partial pressure
Methylene chloride	15	85	0.11	8.7	0.96
Carbon tetrachloride	5	154	0.02	2.3	0.05
Chloroform	5	118	0.03	3.9	0.12
Ethyl acetate	25	88	0.19	1.9	0.36
Acetone	20	58	0.22	4.6	1.01
Ethanol	10	46	0.14	1.2	0.17
Acetonitrile	7	41	0.11	1.9	0.21
Methanol	7	32	0.14	2.5	0.35
Hexane	6	86	0.04	3.0	0.12
True mixture vapor pressure					3.35

[a] All pressures are in psia at 26°C.

F_p, the paint factor, is estimated to be 1.20 for red oxide paint. This is determined from Tables 168 and 170 of the EPA Manual referenced earlier.

C, the small-tank adjustment factor, is taken from Figure 484 of the EPA Manual and is 0.52.

Using the preceding formula, breathing losses were calculated to be 2.63 kg/day (5.8 lb/day) per tank. Maximum total emissions from the two tanks to be ued would be 5.26 kg/day (11.6 lb/day) if uncontrolled. Breathing losses were controlled by venting the storage tanks through an activated charcoal filter system. Adsorption efficiency of the system was conservatively estimated to be 85%. Maximum organic emissions from tank breathing were estimated to be 0.79 kg/day (1.74 lb/day).

Working losses are those losses resulting from tank filling and emptying. During the demonstration, working losses were kept to essentially zero. Most working losses would occur from tank filling if not controlled. However, all vapors expelled from the storage tanks at San Juan Cement during filling were sent into the tank trucks delivering the recycled fuels by means of a hose connecting all tank vents during filling. Because fuels were pumped directly from the tanks into the kiln flame, vapor losses due to tank emptying were minimal and are included in the estimate of breathing losses.

Sizing the activated carbon vapor recovery system entailed several assumptions. The weight of adsorbent required is determined using the following empirically derived equation [6]:

$$W = \frac{teQ_rMC_v}{S(6.43 \times 10^6)} \qquad (3)$$

During the demonstration program MRC replaced an approximately 20-gallon carbon cannister installed by A. T. Kearney with two 55-gallon drums in series filled with activated carbon. Thus, the above equation is then rearranged to calculate the duration of adsorbent service:

$$t = \frac{WS(6.4 \times 10^6)}{eQ_rMC_v} \qquad (4)$$

where t = duration of adsorbent service before saturation, hr

W = weight of adsorbent, lb

e = sorption efficiency (fractional)

Q_r = air flow rate through the sorbent bed, acfm

M = average molecular weight of the sorbed vapor

C_v = entering vapor concentration, ppm by volume

S = proportional saturation of sorbent (fractional)

Table 2-2 presents typical maximum values of retentivities used to estimate S. The sorption efficiency e is a variable determined by the characteristics of the particular system, including concentration and temperature. For the purposes of engineering design calculations it is normally assumed to be 1.0 [6]. Air flow rate Q_r was liberally estimated to be 10 acfm, a value similar to the displacement caused by filling the tanks at 75 gpm. The average molecular weight was taken from the "worst case" volatility example given in Table 2-1, and the vapor concentration was assumed to be 100,000 ppm. With S = 21% and W = 300 lb [7], the duration of service of the two-drum activated carbon vapor recovery system was estimated to be 540 hours, or 22.5 days.

Design and safety recommendations to improve the truck unloading and waste fuel storage module are presented in Section 10.

2.2.3 Waste Pumping and Recirculation Module

The waste pumping and recirculation flow schematic is presented in Figure 2-6. All valving in the lines to and from the feed pump(s) were black iron construction ball valves with stainless steel balls and Teflon seats. A switchable, redundant pair of strainers with a pore size of 0.79 mm (1/32 inch) was used at the pump inlet to catch any solid material in the waste fuel.

TABLE 2-2. RETENTIVITY OF VAPORS BY ACTIVATED CARBON [3] (Percent retained in a dry airstream at 20°C, 101.3 kPa by weight)

Substance	Retentivity, %
Acetone	15
Benzene	24
Carbon tetrachloride	45
Chloroform	40
Ethyl acetate	19
Ethyl alcohol	21
Hexane	16
Isopropyl alcohol	26
Methyl acetate	16
Methyl alcohol	10
Methyl ethyl ketone	25
Methylene chloride	25
Pentane	12
Toluene	29
Water	None
Xylene	34

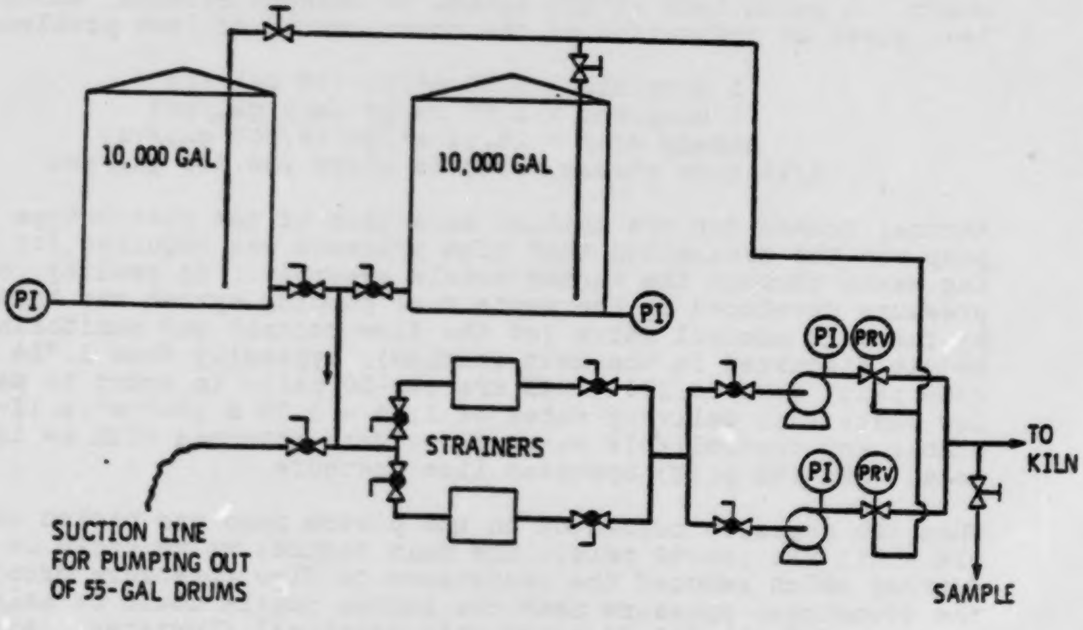
10,000 GAL
10,000 GAL
PI
PI
PI
PRV
PI
PRV
STRAINERS
TO KILN
SUCTION LINE FOR PUMPING OUT OF 55-GAL DRUMS
SAMPLE

Figure 2-6. Waste pumping and recirculation module.

The feed pump used for most of the demonstration program was a redundant pair of belt drive F. E. Myers positive displacement, triple piston-type pumps (Model CX10-15AVAB), capable of developing 10,340 kPa (1,500 psig) and delivering up to 6.31 x 10^{-4} m^3/s (10 gpm). Cylinder bore and stroke distance were both 31.75 mm (1-1/4 inches), and viton O-ring seals were used. Variable pressure relief valves were used on each pump with the low pressure side relieved to a recycle line back into the storage tanks. Dip tubes were used for the recirculation to each storage tank. The high pressure side (feed line) was normally operated at 1,380 - 2,070 kPa (200-300 psig); a pressure gauge was installed on each pump. The feed pumps could be turned on/off from the plant's master control room, and on/off switching was also located outside the storage tank dike area.

Unfortunately, the major application for this type of high pressure pumping system is as a carwash pump, and, consequently, many difficulties and interruptions were experienced in keeping this pumping system operating.

In hazardous fluid pumping applications, positive displacement pumps are generally preferred over centrifugal pumps because 1) they provide positive shut-off when not operating; i.e., the pump serves as a check valve to prevent backflow, and 2) they typically are superior in preventing hazardous material leakage; e.g., most centrifugal pumps require some small amount of leakage to lubricate the interface of the mechanical seal and rotating shaft. A quick look at the extent of leakage effects, shown below, gives an indication of the consequences of leak problems.

1 drop/min = 0.26 m^3/yr (70 gal/yr)
1 drop/sec = 1.59 m^3/yr (420 gal/yr)
steady drip = 15.14 m^3/yr (4,000 gal/yr)
1/16 inch stream = 113.56 m^3/yr (30,000 gal/yr)

Another reason for the initial selection of the piston-type PD pump was the assumption that high pressure was required for feeding waste through the burner nozzle assembly. In reality, high pressure developed by the waste fuel pumping system was throttled by the main control valve (of the flow control and monitoring module discussed in the next section), typically from 1,724 kPa (250 psig) down to 276 - 345 kPa (40-50 psi), in order to maintain low waste fuel delivery rates of 1.26 - 3.79 x 10^{-4} m^3/s (2-6 gpm). Stable and controllable waste flows were obtained with as little as 414 kPa (60 psig) upstream line pressure.

When the pressure regulator on the piston pump was backed off to 414 - 621 kPa (60-90 psig), the main control valve could be opened further which reduced the resistance to flow (pressure drop), and the downstream pressure near the burner nozzle could be maintained at 276 - 345 kPa (40-50 psig) with identical flowrates. Another reason for the lack of need for high pressure is the burner nozzle design and requirements for waste fuel spray pattern, which will be discussed in the burner assembly module section.

Therefore, with the subsequent elimination of the need for of a high pressure waste requirement, the need for a high pressure piston, diaphragm, or gear pump disappears. A simple, durable, reliable centrifugal-type pump can more efficiently accomplish the job. Design and safety recommendations on pump selection, maintenance, and leak-proofing follow in Section 8.

2.2.4 Flow Control and Monitoring Module

The flow control and monitoring module was installed adjacent to the burner assembly at the hot end of the kiln. Figure 2-7 illustrates the components of the flow monitoring module. All piping and fittings were Schedule 80[a] black iron construction. All of the ball valves were 19 mm (3/4 inch) Apollo ball valves with black iron body, stainless steel ball, and Teflon seat. Where the waste fuel feed line enters the area, a ball valve was used to provide positive system shutoff. Following that valve is the automatic emergency shut-off valve which is wired into the fuel oil feed system such that loss of adequate burning zone temperature due to cut-off in fuel oil would automaticaly shut off the waste fuel feed. A pressure indicator and temperature indicator monitor the waste fuel in front of the main flow control valve, which was a Hancock gate valve of black iron construction. Downstream from the control valve were three different flow monitoring devices. A Brooks Instrumenter oscillating piston-type totalizing flow meter, cast iron construction, was used to provide an integrated accounting of the amount of waste fuel burned. A Fisher & Porter magnetic flow meter was used to provide a visual, instantaneous readout of liquid flow rate and aid in setting the main control valve. Calibration of this flowmeter was given by the manufacturer in terms of specific gravity of the fluid passing through the flowmeter. A Calibrated Taylor flow element orifice meter was also used as a backup to provide instantaneous flow rates and could be monitored in the control room through pneumatic signal transmission coupled to a circular chart recorder. All three of the flow metering devices were rated for operation over the range of 6.31×10^{-5} to 9.47×10^{-5} m^3s (1 to 15 gpm). A final ball valve was inserted into the feed line as a redundant shutoff, then another pressure indicator to monitor the pressure drop across the control valve and flow meters. This pressure indicator gave the final reading of the fluid pressure delivered to the burner nozzle. A stainless steel flexline was used to connect the feed monitoring system to

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[a] Schedule 80 was selected on the presumption that the waste had to be pressurized to 300 psig. Schedule 40 will suffice for pressures below 160 psig.

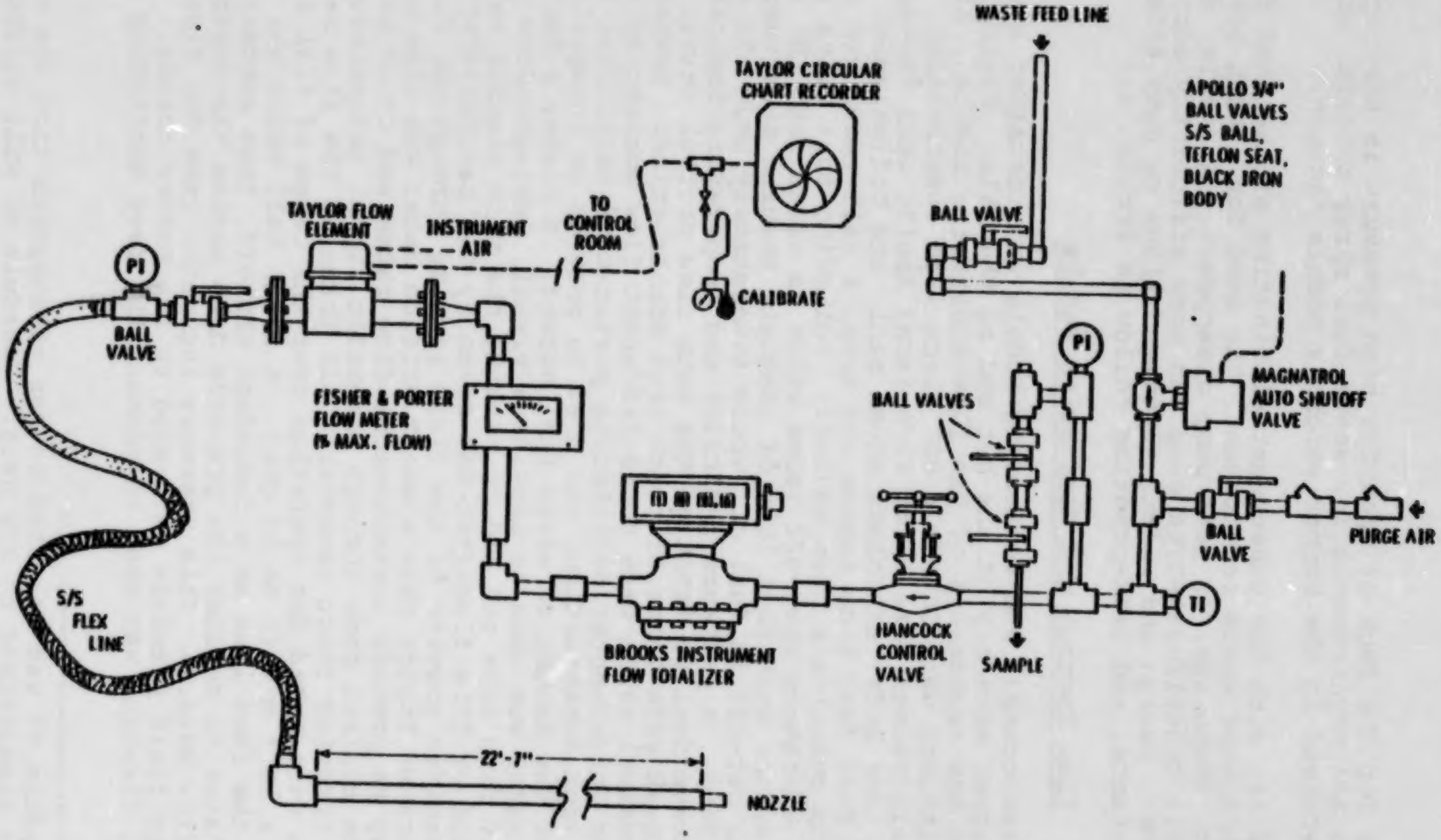
WASTE FEED LINE
TAYLOR CIRCULAR CHART RECORDER
APOLLO 3/4" BALL VALVES S/S BALL, TEFLON SEAT, BLACK IRON BODY
BALL VALVE
TAYLOR FLOW ELEMENT
INSTRUMENT AIR
TO CONTROL ROOM
PI
CALIBRATE
BALL VALVE
PI
BALL VALVES
MAGNATROL AUTO SHUTOFF VALVE
FISHER & PORTER FLOW METER (% MAX. FLOW)
BALL VALVE
PURGE AIR
S/S FLEX LINE
BROOKS INSTRUMENT FLOW TOTALIZER
HANCOCK CONTROL VALVE
SAMPLE
TI
22'-7"
NOZZLE

Figure 2-7. Flow control and monitoring module schematic.

the burner nozzle assembly. Purge air was provided after the auto shutoff valve to blow out waste fuel from the module line after waste fuel shutdown so that the burner nozzle assembly could be removed from the kiln without spilling hazardous waste. Purge air was also used to cleanse all feed lines to the pumps (about 61 m) so that system leaks could be repaired.

2.2.5 Burner Nozzle Assembly

The burner gun and nozzle assembly for waste fuel was mounted inside the kiln's existing fuel oil burner assembly, depicted in Figures 2-8 and 2-9. The entire burner assembly consists of a fuel oil gun (tube) which runs along the centerline of the assembly with primary air flowing concentric to the fuel oil. The waste fuel gun runs parallel to the fuel oil gun but slightly off centerline, as shown in the end view in Figure 2-10. The nozzle hole size for fuel oil is 10 mm diameter in 51 mm diameter rod and delivers 1.58×10^{-3} m^3/s (25 gpm) to the flame. The waste fuel gun was 42 mm in diameter and the stainless steel nozzle assembly screwed into the end of the gun.

The waste fuel nozzle design in the initial phase of the program, incorporated an adjustable (by means of spacer rings) needle to aid in feed atomization. This atomization was found to be undesirable because a very narrow spray pattern is required to keep the flame off the kiln walls and the spray pattern must reach out into the fuel oil flame. The nozzle design which satisfied the kiln operators and pushed a narrow stream of waste fuel into the fuel oil flame is shown in Figure 2-11.

The No. 6 fuel nozzle design was very simply a 10 mm (0.3937 in.) constriction in the fuel oil feed gun. The fuel oil flame was typically 1.22 to 3.05 m (4 to 10 ft) off the nozzle tip, with unburned oil visible through the kiln's viewing port and shown in Figure 2-12. This is termed "suspended-flame combustion" when the flame is kept well away from the throat, diffuser, and fuel nozzle, thus eliminating maintenance due to flame impingement.

The kiln operators preferred that the waste fuel flame also be separated from the nozzle tip because if the waste fuel flame returned to the nozzle tip it tended to pre-ignite the fuel oil and upset the control of the burning zone temperature. At San Juan Cement the kiln is operated with an axial discharge velocity which is greater than the flame speed of 33.5 m/s as estimated during kiln operation.

The axial discharge velocity from a nozzle can be calculated from the pressures, p_1 at entry and p_2 at exit, and the density, ρ, of the liquid:

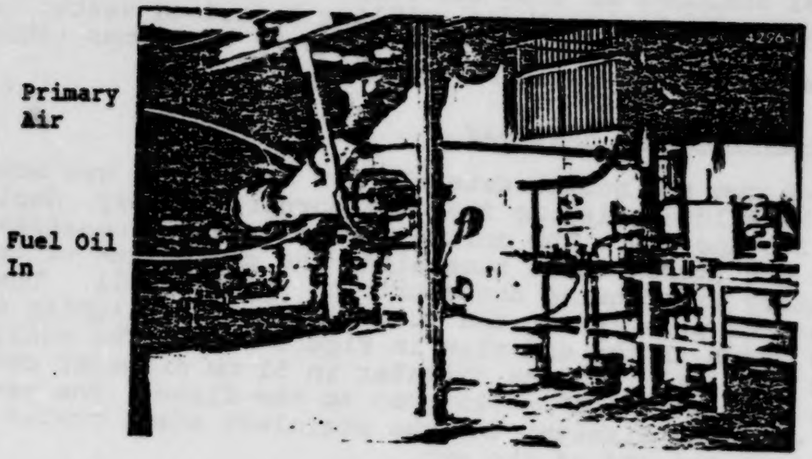
Primary Air
Fuel Oil In
4296-1

Figure 2-8. Fuel oil burner assembly at kiln #2, San Juan Cement Co., Dorado, Puerto Rico.

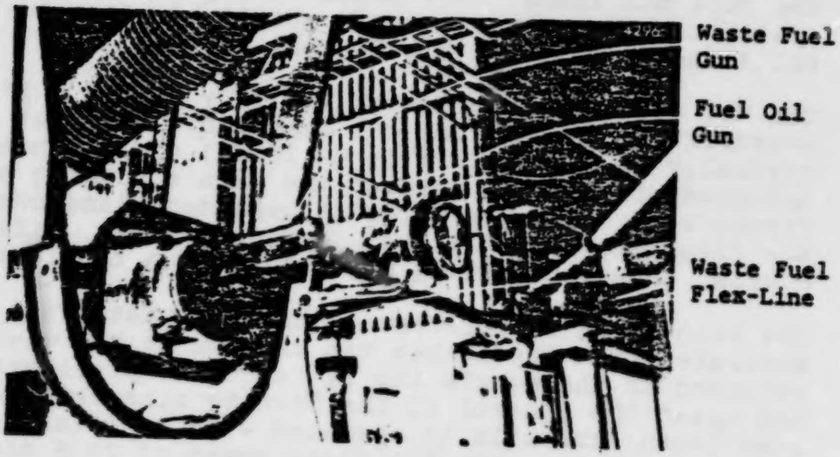
Waste Fuel Gun
Fuel Oil Gun
Waste Fuel Flex-Line

Figure 2-9. Fuel oil control valve and location of waste fuel gun, San Juan Cement Co., Dorado, Puerto Rico.

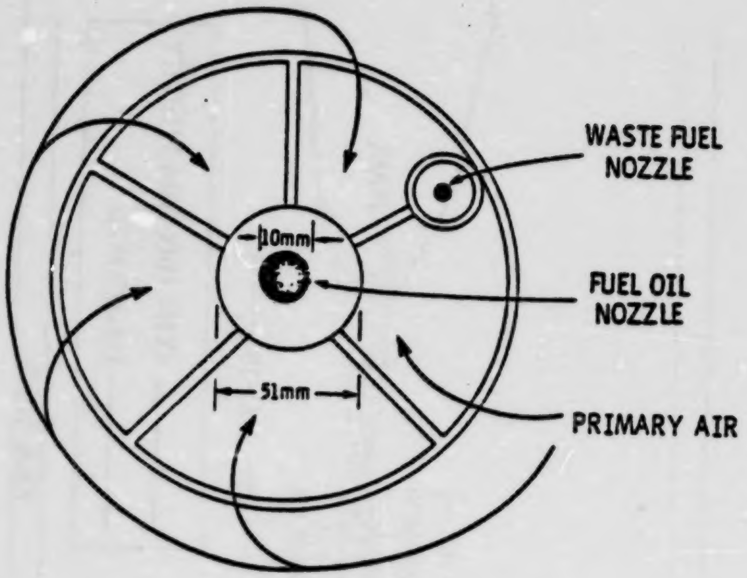
WASTE FUEL NOZZLE
10mm
FUEL OIL NOZZLE
51mm
PRIMARY AIR

Figure 2-10. End view of kiln #2 fuel oil nozzle and burner assembly.

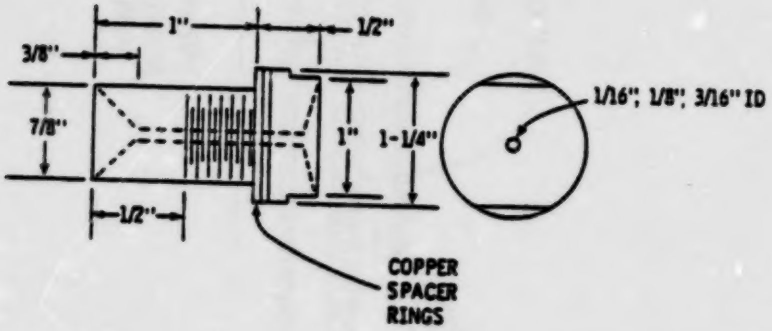
1"
1/2"
3/8"
7/8"
1"
1-1/4"
1/2"
1/16", 1/8", 3/16" ID
COPPER SPACER RINGS

Figure 2-11. Waste fuel nozzle design used for demonstration burn at San Juan Cement Company.

$$V_a = c\sqrt{\frac{2g(p_1 - p_2)}{\rho}} \qquad (5)$$

where c is the coefficient of discharge of the nozzle or atomizer, and varies in value for different atomizers and for different conditions of flow [8]. It can be determined experimentally by

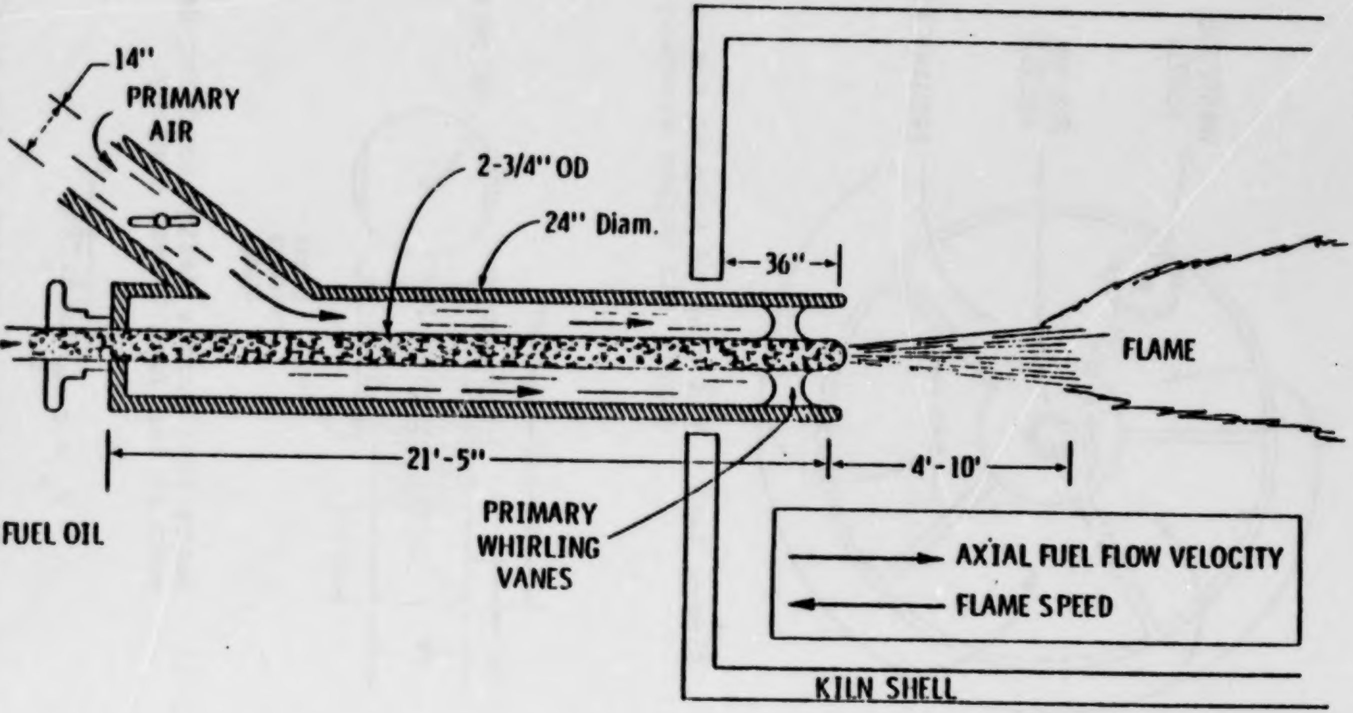
14"
PRIMARY AIR
2-3/4" OD
24" Diam.
36"
FLAME
21'-5"
4'-10'
FUEL OIL
PRIMARY WHIRLING VANES
AXIAL FUEL FLOW VELOCITY
FLAME SPEED
KILN SHELL

Figure 2-12. Representation of the oil flame configuration.

measuring the volume of liquid discharged from an atomizer of known orifice size, during a given time interval and with a given pressure drop:

$$Q = avt = atc\sqrt{\frac{2g\Delta p}{\rho}} \qquad (6)$$

from which

$$c = \frac{Q}{at\sqrt{\frac{2g\Delta p}{\rho}}} \qquad (7)$$

where Q is the volume of liquid, a is the area of the orifice, and t is the time. The value of the coefficient c is typically 0.8 to 0.95 for plain atomizers, and is very much lower (0.2 to 0.6) for swirl atomizers, in which a greater part of the fuel energy appears as tangential velocity [8].

Four different waste fuel nozzle orifice diameter sizes were tested during the demonstration burn program: 1.59 mm (1/16 in.), 3.18 mm (1/8 in.), 3.97 mm (5/32 in.), and 4.76 mm (3/16 in.). The 1.59 mm orifice nozzle plugged almost immediately with particles contained in the waste fuel and/or char formed from the burning fuel. It is recommended that the 1.59 mm orifice nozzle not be used. The 3.18 mm orifice gave a maximum flow rate of 3.00×10^{-4} m^3/s (4.76 gpm) with a feed line pressure of 2.76 kPa (40 psig) and a waste fuel of 0.9948 specific gravity. It was observed that at 3.00×10^{-4} m^3/s the flame did not remain on the nozzle tip but oscillated from the tip to about three feet off the tip. The axial discharge velocity at this condition is about 38.1 m/s. At a flow rate of 2.84×10^{-4} m^3/s the flame returned to the burner tip, which corresponds to an axial discharge velocity equal to the flame speed, or about 33.5 m/s.

The 4.76 mm orifice nozzle could obtain a maximum flow rate of 6.25×10^{-4} m^3/s (9.9 gpm) at 276 kPa (40 psig). When the flow rate through this orifice was decreased to 1.26×10^{-4} m^3/s (2.0 gpm), some waste fuel failed to reach the oil flame and dripped onto the floor of the kiln. This mode of operation is undesirable for 1) the kiln operator because high, localized kiln shell temperatures and poor quality clinker result, and 2) the destruction efficiency of the waste fuel is decreased because poor atomization results and contact with the burning zone is decreased. When the flow rate through the 4.76 mm orifice was increased to 1.89×10^{-4} m^3/s (3.0 gpm), the dripping stopped and the flame burned at the nozzle tip. The dripping occurred at an axial discharge velocity of about 7.0 m/s and stopped at 10.7 m/s. Thus, an axial discharge velocity of 10.7 m/s is the recommended minimum for retaining the waste fuel in the kiln's burning zone, although a much higher discharge velocity is needed to push the waste fuel flame in line with the oil flame.

Based on operating experience the recommended waste fuel feed rates to the kiln for various sized nozzle orifice diameters are presented in Table 2-3.

TABLE 2-3. MINIMUM AND MAXIMUM WASTE FUEL FEED RATES AS A FUNCTION OF NOZZLE ORIFICE SIZE

Nozzle orifice diameter, mm (in.)	Waste fuel feed rate, m^3/s (gpm) minimum	maximum
1.59 (1/16)	–[a]	–[a]
3.28 (1/8)	8.46×10^{-5} (1.34)	3.00×10^{-4} (4.76)
3.97 (5/32)	1.32×10^{-4} (2.09)	4.34×10^{-4} (6.87)
4.76 (3/16)	1.91×10^{-4} (3.02)	6.25×10^{-4} (9.91)

[a] Do not use; plugging occurs.

SECTION 3

SAMPLING AND ANALYSIS PROGRAM DESIGN AND TEST MATRIX

The sampling and analytical program was designed to identify all major pollutants from the burning of the hazardous wastes available for this program and to quantify their respective emission rates, investigate the chlorine material balance of the cement process, determine burning rate limits as related to product acceptability and refractory lining integrity, and determine the destruction and removal efficiencies (DRE) of the principal organic hazardous constituents (POHCs) in the waste fuels. Emission measurements included particulate matter, carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), nitrogen oxides (NO_x), hydrogen chloride (HCl), total gaseous hydrocarbons (THC), total chlorinated hydrocarbons, methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), trace metals in particulate matter, organics with special attention given to dioxins and dibenzofurans, high molecular weight ($>C_6$) organics, volatile organic fraction species in process water, and trace metals, organics, dioxins, and furans in the baghouse flyash. Chlorine content of the baghouse flyash and cement clinker were also monitored. The waste fuels and fuel oil used to fire the cement kiln were analyzed for principal organics, trace metals, ash, chlorine, nitrogen, and sulfur content.

Table 3-1 summarizes the overall test program and shows each collection method and analytical method.

Table 3-2 summarizes the experimental test matrix of the demonstration program wherein the waste feed rate to the kiln and the chlorine content of the waste were varied.

3.1 WASTE ANALYSIS

A Hewlett-Packard 5982 mass spectrometer, interfaced to a Hewlett-Packard 5830 glass capillary gas chromatograph operated in the split injection mode, was used to analyze for the major components of the waste fuel samples. This is what is commonly termed "wide scan organic analysis."

TABLE 3-1. SAN JUAN CEMENT COMPANY WASTE FUEL DEMONSTRATION BURN SAMPLING AND ANALYTICAL PROGRAM

Parameter measured	Sampling method	Analytical method
Stack Samples		
Particulate matter	EPA Method 5	EPA Method 5
Metals on particulate	EPA Method 5	ICAP
Organics on particulate	EPA Method 5	Extractions and GC/MS for principal organics, dioxins, and furans
Opacity	EPA Method 9	EPA Method 9 (on site)
Sulfur dioxide	EPA Method 6	EPA Method 6
Nitrogen oxides	EPA Method 7	EPA Method 7
Carbon monoxide	EPA Method 10	NDIR continuous analyzer
CO_2 and O_2	Integrated bag sample	EPA Method 3 (on site)
Hydrogen chloride	Impinger train	Specific ion electrode
Total gaseous hydrocarbons	Direct to analyzer	Continuous FID
Total chlorinated hydrocarbons	Integrated bag samples	GC/EC (on site)
Three chloinated species (POHC's)	Integrated bag samples	GC/EC (on site)
Organic compound speciation	SASS train	GC/MS
Ambient Air		
Particulate matter	High volume gas sampler	EPA-Appendix B FR 121:0105
Process Water		
Organics (3 species)	Integrated sample	EPA priority pollutant methodology, GC/MS
No. 6 Fuel Oil		
Btu content	Grab	ASTM D240-64
Chlorinated methanes	Grab	GC/EC
Sulfur content	Grab	ASTM D-3177
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
Waste fuel		
Btu content	Grab	ASTM D240-64
Moisture content	Grab	GC/MS
Total chlorine	Grab	ASTM D6081
Total nitrogen	Grab	Kjeldahl
Total sulfur	Grab	ASTM D129
Trace metals	Grab	ICAP
Principal organics	Grab	GC/MS
PCBs and pesticides	Grab	GC/MS and GC/EC
Ash content	Grab	ASTM D482-IP4
Solid Waste (kiln dust)		
Principal organics	Grab	Extraction and GC/MS
Furans and dioxins		
Chlorine content	Grab	ASTM D-808
E.P toxicity	Grab	
Furans and dioxins		Extraction and GC/MS
Trace metals		ICAP

TABLE 3-2. EXPERIMENTAL TEST MATRIX OF WASTE FEED RATE AND CHLORINE CONTENT

Approximate waste feed rate to kiln, m^3/s (gpm)	Percent chlorine in waste, wt %						
	6.5	10.1	18.7	21.4	22.9	32.0	35.1
8.39×10^{-5} (1.33)		x					
9.46×10^{-5} (1.50)	x		x				
1.10×10^{-4} (1.75)			x				x
1.26×10^{-4} (2.00)		x		x			
1.89×10^{-4} (3.00)						x	
2.21×10^{-4} (3.50)		x		x			x
2.71×10^{-4} (4.30)				x			
3.15×10^{-4} (5.00)					x	x	
3.47×10^{-4} (5.50)		x					
3.79×10^{-4} (6.00)		x					

x = conditions tested.

The waste fuel samples were diluted 1:10 in o-xylene before introduction to the $(GC)^2/MS$ system. Method of identification was by means of mass spectra alone (MS) or mass spectra and retention time (MS, RT). Each detected component was quantified relative to a standard volume of that component injected into the $(GC)^2/MS$ or another compound which eluted in the vicinity of that compound.

The sum total of all the volume percents reported typically ranged from 85 to 93%, rather than 100%. This discrepancy results because the response of the spectrometer is nonlinear for some compounds, which gives a lowered value; some portion of the waste fuel is nonchromatographable and is not seen by the instrument, e.g., higher molecular weight alcohols; and a small portion of the waste fuel is a solid residue.

For two of the seven waste batches the chlorinated hydrocarbons known to be present in the waste fuel -- methylene chloride, chloroform, and carbon tetrachloride -- were additionally analyzed by gas chromatography with an electron capture detector (GC/EC) to confirm the $(GC)^2/MS$ results. The quantification of these three chlorinated compounds was vital for an accurate calculation of the cement kiln's destruction and removal efficiency (DRE). EC detectors typically show better response to halogenated organic components than other techniques.

In order to safeguard public health, the Puerto Rican Environmental Quality Board banned the burning of polychlorinated biphenyls (PCBs) and pesticides as one of the conditions of the temporary operating permit.

Analysis of the waste fuel samples for the presence of PCBs and pesticides (per the Priority Pollutant list) was done on a glass capillary GC/MS using the Selected Ion Monitoring (SIM) mode. Levels of detection for individual PCB isomers were on the order of 0.5 ppm at the instrument. Since the samples were diluted 1:10 before injection, this corresponds to a level of detection in the waste fuel sample of 5 ppm. Total PCBs, the sum of all possible isomers, had a level of detection of less than 50 ppm. For pesticides, level of detection was at or above 100 ppm.

The Btu content of the waste fuel samples was determined by ASTM D240-64, which is a Parr bomb technique. Ash content of the waste fuel was determined by ASTM D482-IP4, and specific gravity at 25°C by the calibrated dilatometer method.

ASTM analytical methods were also used on selected waste fuel samples to determine the sulfur, nitrogen, and chlorine content for comparison with $(GC)^2$/MS.

The trace metal content of the waste fuels was determined by EPA Interim Method 200.7, which is dilution in xylene followed by analysis using inductively coupled argon plasma emission spectroscopy (ICP). The ICP method is an analytical system for simultaneous multielement determinations of trace metals at the sub-ppm level in solutions.

3.2 WASTE INTEGRITY

All of the waste fuels used during the demonstration program came from pharmaceutical industries in Puerto Rico, were specifically blended for the demonstration by a waste recycling firm, and were transported to San Juan Cement by a hazardous waste truck tanker. In general, the waste fuels were a nonchlorinated distillate fuel fraction (reclaimed solvents) blended with a chlorinated solvent (degreaser) mixture to achieve various levels of chlorine content.

3.2.1 WASTE ACQUISITION AND TRANSPORTATION

Before a candidate waste fuel was accepted at San Juan Cement, the recycling firm conducted a gas chromatographic (GC/FID) analysis to determine the composition of the waste batch. Upon arrival at the cement plant and before loading into the storage tanks, MRC conducted an immediate GC/FID analysis to confirm the identity of the waste shipment. This was performed in the laboratory on a one-week turnaround basis for a more detailed gas chromotograph-mass spectrometer $(GC)^2$/MS analysis and capillary GC/MS, and upon arrival of the waste the on-site GC/FID analysis was used to confirm the earlier GC/MS analysis. No waste fuels were burned which had not been analyzed.

3.2.2 STORAGE TANK MANIFEST SYSTEM

At each of the two storage tanks a liquid waste storage tank log was kept in a sealed plastic cover and attached to the tank's main valve. the first part, shown in Figure 3-1, described the chemical composition of the waste stored in that tank, and the second part, shown in Figure 3-2, described additions, withdrawals, dates, and other inventorial information such as leakage between the tanks.

This system allowed any interested personnel to ascertain rapidly what was contained in the tank and the history pertaining to the current content level.

3.3 LOCATION OF SAMPLING POINTS

The testing site was the exhaust stack serving the baghouse of Kiln #2, as shown in Figure 3-3. The stack is 17.7 m (58 ft) high, mounted on a cement base, 2.7 m (9 ft) in diameter, with a sampling platform about 14.9 m (49 ft) high serving four 102 mm (4-in.) sampling ports. The ports are located 3.55 diameters from the nearest upstream disturbance (the junction of ID fan ductwork to the stack) and 0.63 diameters from the nearest downstream disturbance (stack oulet). In accordance with EPA Method 1 criteria, a traverse of 48 sample points (24 in each of two ports 90° apart) was used for EPA Method 5 particulate runs at 2 minutes/point. The remaining two ports were used for the SASS train, HCl sampling, and EPA Methods 6 and 7 sampling.

A third sample port was installed about 5.5 m (18 ft) up the stack, as shown in Figure 3-3, from which gaseous samples were taken for analysis inside the laboratory trailer. A stainless steel wire mesh filter was placed inside the stack, and a heated Teflon sample line (175°C) carried the gas sample to a heated manifold (175°C). Continuous vacuum by means of an air aspirator was used on the sample line to keep sample gas flowing through the system at 1.4×10^{-3} m^3/s (~3 cfm).

Figure 3-4 illustrates the sampling platform area, which was somewhat small. Modifications made included the construction of monorails for the samplers, removal and welding of portions of the platform handrails to accommodate equipment movement, a gantry for raising and lowering equipment, providing electrical power and lighting, and protective covering against rain and sun. Upgrading of the stack area by San Juan Cement Company included improving the stack insulation around the platform area and modernizing the ladder to the platform. Figures 3-5 and 3-6 give two views of the stack sampling area.

The air-conditioned laboratory trailer was located at the base of the stack, and had the heated gas sample line, SASS line, and EPA Method 5 umbilical gas line running into it. Figure 3-7

LIQUID WASTE STORAGE TANK LOG

☐ North Tank

☐ South Tank

COMPONENT	WASTE ANALYSIS RECORD		
	Per Supplier Manifest	Per On-Site GC/FID Analysis	Per Laboratory GC/MS Analysis
Water, %			
Methanol, %			
Ethanol, %			
Acetone, %			
Methylene Chloride, %			
Isopropanol, %			
Hexane Isomers, %			
Pentane, %			
n-Hexane, %			
Chloroform, %			
Ethyl Acetate, %			
Acetonitrile, %			
Acrylonitrile, %			
Carbon Tetrachloride, %			
Benzene, %			
Toluene, %			
PCB, ppm			
Pesticides, ppm			
Herbicides, ppm			
ELEMENT			
Carbon %			
Hydrogen %			
Chlorine, %			
Nitrogen, %			
Oxygen, %			
Water, %			

Heating Value, BTU/lbm =

Figure 3-1. Waste fuel manifest to determine identity of storage tank contents.

LIQUID WASTE STORAGE TANK LOG

☐ North Tank

☐ South Tank

INVENTORY RECORD

Date	Additions, Gal.	Withdrawals, Gal.	Inventory, Gal.	Comments	Name

Figure 3-2. Waste fuel manifest to determine history of storage tank contents.

withdrawals, dates, and other inventorial information such as leakage between the tanks.

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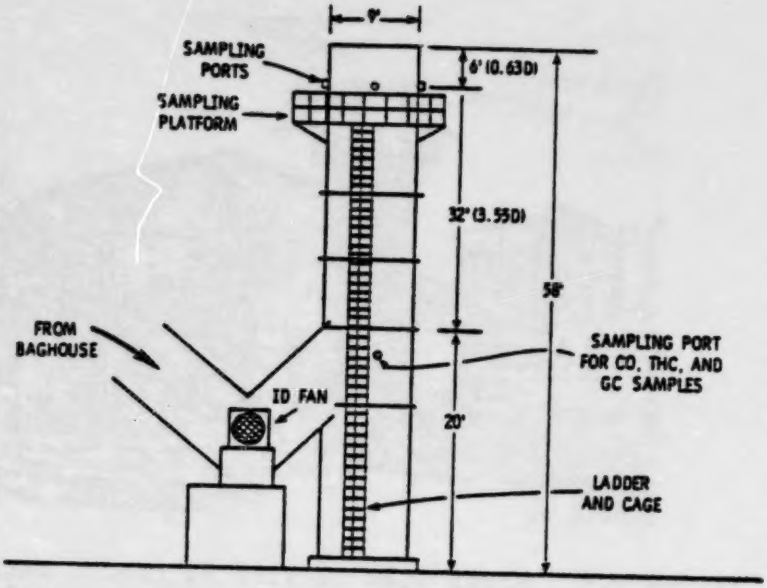

9'
SAMPLING PORTS
SAMPLING PLATFORM
6' (0.63D)
32' (3.55D)
58'
FROM BAGHOUSE
SAMPLING PORT FOR CO, THC, AND GC SAMPLES
ID FAN
20'
LADDER AND CAGE

Figure 3-3. Schematic diagram of Kiln #2 exhaust stack, east view, San Juan Cement Company, Dorado, Puerto Rico.

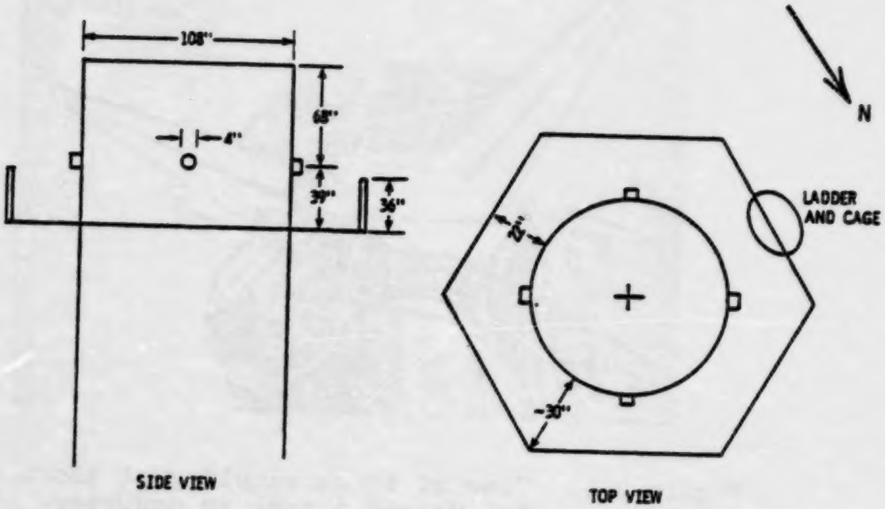

108"
68"
4"
39"
36"
N
LADDER AND CAGE
~30"
SIDE VIEW
TOP VIEW

Figure 3-4. Schematic diagram of Kiln #2 stack sampling platform, San Juan Cement Company, Dorado, Puerto Rico.

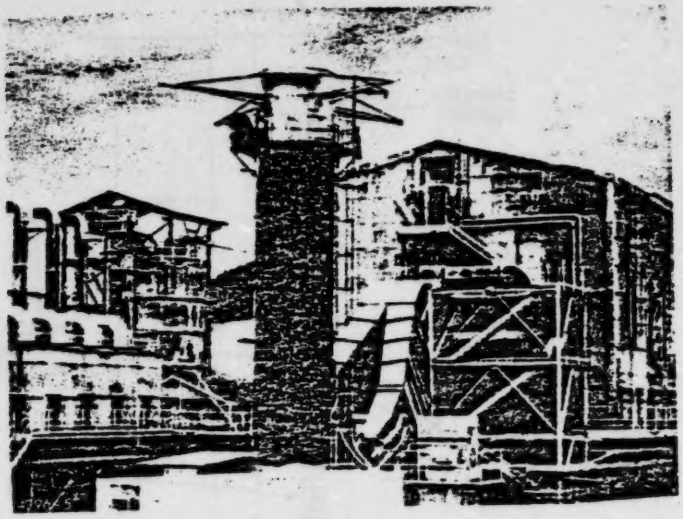


Figure 3-5. North view of Kiln #2 stack, baghouse, and laboratory and storage trailers.

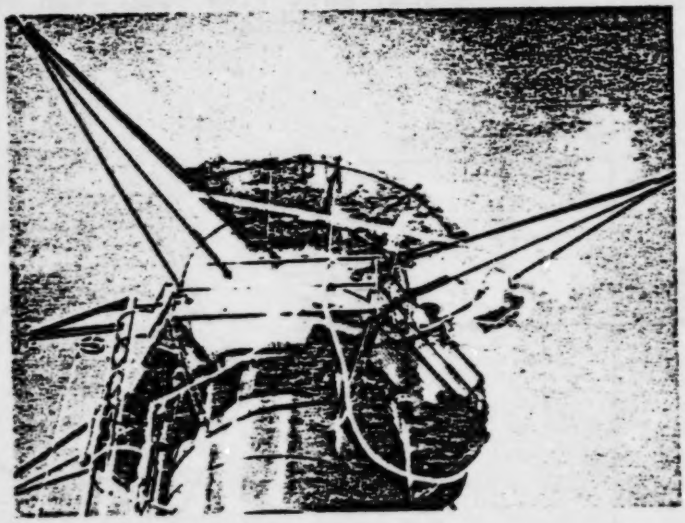
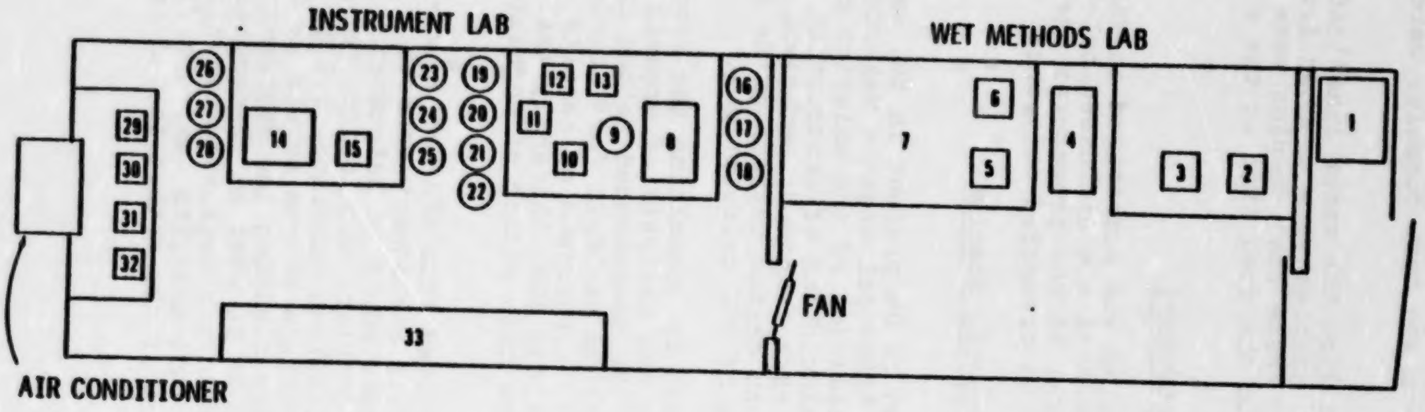


Figure 3-6. View of stack sampling platform with EPA Method 5 test in progress.


INSTRUMENT LAB
WET METHODS LAB
FAN
AIR CONDITIONER
1
2
3
4
5
6
7
8
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13
14
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1. REFRIGERATOR
2. METHOD 5 CONSOLE
3. SASS CONSOLE
4. SASS COOLING SYSTEM
5. SASS ORGANIC MODULE
6. SASS IMPINGER BOX
7. TRAIN PREPARATION AREA
8. GC/FID FOR WASTE FUEL ANALYSIS
9. GAS SAMPLE MANIFOLD
10. CO ANALYZER (NDIR)
11. RECORDER - CO ANALYZER
12. PRETREATER - CO ANALYZER
13. AUTOCALIBRATOR - CO ANALYZER
14. THC ANALYZER - FID
15. RECORDER - THC ANALYZER
16. H_2 GAS FOR GC/FID
17. ZERO AIR FOR GC/FID
18. N_2 FOR GC/FID
19. ZERO AIR FOR CO ANALYZER
20. STD. GAS - 310 ppm CO
21. STD. GAS - 605 ppm CO
22. STD. GAS - 897 ppm CO
23. ZERO AIR FOR THC ANALYZER
24. STD. GAS - 3 ppm CH_4
25. STD. GAS - 44 ppm CH_4
26. GC/EC FUEL GAS - 95% ARGON/5% H_2
27. THC FUEL GAS - 40% H_2/60% N_2
28. GC/EC CARRIER GAS - He
29. GC/EC CALIBRATOR - DYNAMIC PERMEATION
30. GC/EC CALIBRATOR - DYNAMIC DIFFUSION
31. GC/EC
32. H-P INTEGRATOR
33. NO_x FLASK STORAGE

Figure 3-7. Schematic layout of field sampling laboratory trailer, San Juan Cement Company.

illustrates the lab trailer layout; gas analyzers were contained in one room and the sample work-up and test consoles were kept in the other room.

Process water samples were taken from the water line leading to the Kiln #2 area. Baghouse dust samples were grabbed from the conveyor emptying the baghouse. Waste fuel samples were grabbed from a sampling valve inserted in the feed line at the control valve area (see Figure 2-7.)

3.4 SAMPLING AND ANALYTICAL PROCEDURES

The sampling and analytical program was summarized in Table 3-1. The details of the program procedures are discussed below. Because the baseline testing was identical to the procedures used during the test burns, the methodology is presented only once.

3.4.1 POHC'S and Chlorinated Organic Species

3.4.1.1 Selection of Method--

Three chlorinated methanes known to be present in the waste fuel batches were designated as the Principal Organic Hazardous Constituents (POHC's). Quantification of the emission rate of the POHC's was vital for the calculation of destruction and removal efficiencies (DRE) for each compound: methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). Section 5 contains a discussion of DRE calculations.

The method of analysis was chosen by consulting the Procedures Manual for EPA Level 2 sampling and analysis of organic materials, in particular, alkyl halides. The recommended method is GC/MS with a suggested alternative method of GC/EC for interference free samples [9]. Because rapid turnaround of results was desired for the program by the Puerto Rican EQB, the analytical method using a GC/EC was chosen because this method of chromatography is field portable.

Additional consultation was derived from EPA Method 23-Determination of Halogenated Organics From Stationary Sources. This validated method applies to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1,1,1,-trichloroethane, and trichlorotrifluoroethane at ppm levels in stack gases of vinyl chloride plants and dry cleaning and degreasing facilities. The principle of Method 23 is that an integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID). The range of the method is 0.1 to 200 ppm (10).

For field portability the flame ionization detector (FID) is the most versatile general purpose gas chromatography device. The FID responses to any substance that will burn in the air/hydrogen flame to produce ions. Most organics, except for highly halogenated species, give strong FID responses. The lower limit of detection for organic species is on the order of one nanogram per microliter (1 ppm) of injected solution, and the dynamic range of the FID detector spans four or more orders of magnitude [9].

The electron capture detector (EC) is specific for species that contain electronegative atoms or groups -- halogens, phosphorus, sulfur, and nitro groups. The lower limit of detection is as much as 1000 times lower than that of the FID, but the dynamic range is generally smaller. The magnitude of the EC response is sensitive to analyte structure, as well as to concentrations, since different species have different election capture cross sections [9].

In previous reporting on cement kiln incineration tests, it was found that at the Stora Vika tests in Sweden a waste was burned which contained methylene chloride and trichloroethylene. Gas collection was by an isokinetic glass sampler (similar to EPA Method 5), through cooled water-containing impingers, then through an absorption column containing APIEZON M®, where heavier chlorinated substances were absorbed, and finally through a second column filled with activated charcoal, where lighter chlorinated hydrocarbons were extracted [11]. Analysis was via solvent extraction and GC/EC.

In the Canadian tests at St. Lawrence Cement Company, Chromosorb 102 tubes were used for gas collection, followed by thermal desorption, and GC/EC for quantification. This method worked well and ranges from 0.0004 to 29 ppb were reported for CH_2Cl_2, $CHCl_3$, and CCl_4 when burning wastes containing a variety of chlorinated hydrocarbons [12]. A thermally desorbed sample, however, is expended and the analyst is unable to perform replicate analyses on a selected single sample. Solvent desorption will allow for replicate analyses (provided the detection limit is not comprised), but the technique is much more time consuming and less suitable in a field laboratory situation.

Thus, it was chosen that gas bag samples would be collected for immediate analysis by GC/EC in a field laboratory. This method allowed for anticipated ppb quantification, replicate analyses, reference to external calibration standards, and rapid turnaround of results.

3.4.1.2 Integrated Gas Sample Collection--
Each testing day, two to seven (typically 4-5) integrated gas samples were collected from the heated gas sampling manifold into Teflon FEP (Type A) gas bags. The gas collection bags

were Alltech Associates CRP Sampling Bags which were manufactured in a Class 100 clean room to meet NASA specification #MSC-C-25 Level 1 for use in trace gas analysis. All seams had been tested with filtered dry nitrogen at an inflation pressure of 34.5 kPa (5 psig). Integrated sampling periods to fill each bag ranged from 10 to 50 minutes, typically 30 minutes. A metal bellows pump, identical to that used in an EPA Method 6 train, pulled the gas sample through a calcium chloride drying tube to remove moisture, as shown in Figure 3-8. Calcium chloride desiccant is preferred over other desiccants in reducing absorption of chlorinated hydrocarbons.

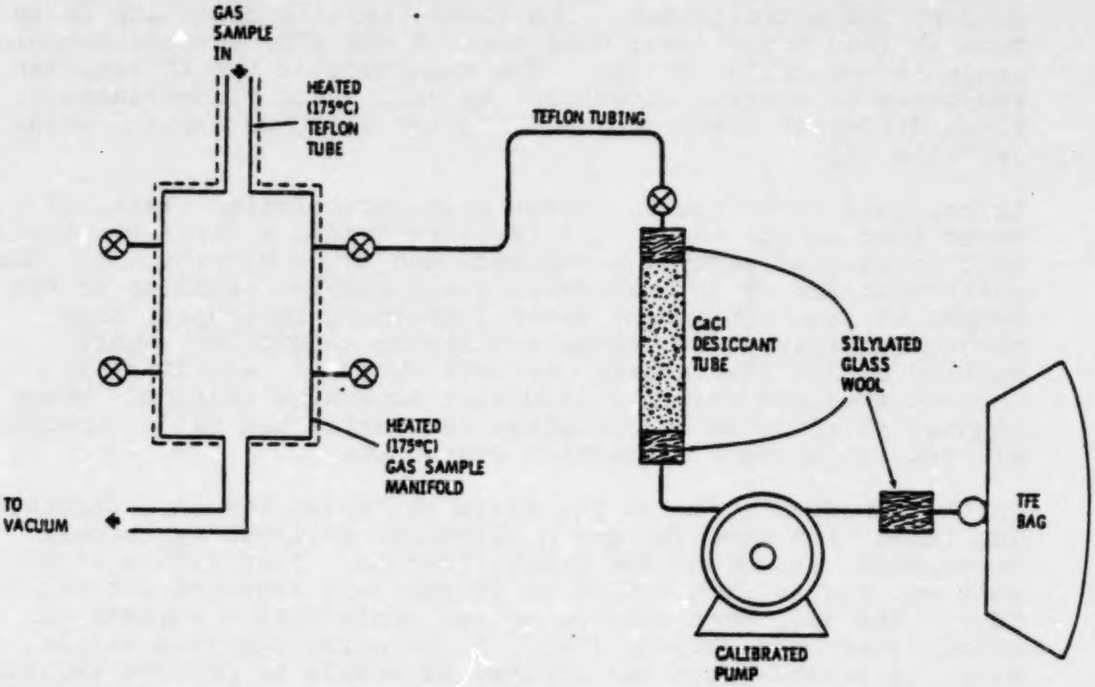

GAS SAMPLE IN
HEATED (175°C) TEFLON TUBE
TEFLON TUBING
CaCl DESICCANT TUBE
SILYLATED GLASS WOOL
HEATED (175°C) GAS SAMPLE MANIFOLD
TO VACUUM
TFE BAG
CALIBRATED PUMP

Figure 3-8. Schematic diagram of integrated bag sample train for GC analysis.

Each sample bag was kept out of direct sunlight, maintained within an air-conditioned room, and the analysis was performed within one-half hour of sample collection. After analysis, the bag was purged 3-5 times with dry nitrogen and valve closed for re-use. An in-field study was conducted to compare chlorinated hydrocarbon contamination between purged bags and new bags, and GC/EC results indicated no difference. A bag was discarded when visible moisture was present inside the bag.

3.4.1.3 GC/EC Analysis--

Gas sample analysis was conducted in the laboratory trailer with an AID Model 511 portable gas chromatograph equipped with the Analysis Option 06 electron capture detector assembly. The detector utilizes a 200 millicurie Tritium foil to provide an ion current. Electron capturing species that elute from the chromatographic column reduce this current and generate a signal. To maximize the detector performance a pulsed potential (28V, 1 μsec width, 35 μsec interval) is applied across the parallel plates of the detector. The detector was operated at 75°C with an injection temperature of 70°C.

The chromatographic column was an AID 10% by weight DC-200 supported on 80/100 mesh Chromosorb WHP (1.8 m x 3.2 mm). The GC sampling system was a 1 mL stainless steel sample loop, which was allowed to return to atmospheric pressure before injection.

The minimum detectable amount, as specified by the manufacturer, is 1 pg CCl_4 in a 1 mL air sample (0.2 ppb CCl_4). On a new Tritium source detector the maximum deflection is 80% of full scale, as measured by the standing current test. At San Juan Cement the measured standing current deflection was 22% (four separate tests), which was also measured at 22% at the Dayton Laboratory prior to equipment shipment. The decreased standing current deflection is due to detector source aging. This four-fold reduced sensitivity alters the detection limit for CCl_4 by approximately four-fold, or 0.8 ppb. Similarly, the manufacturer's minimum detectable value for chloroform ($CHCl_3$) is 10 ppb. Correcting four-fold for source degradation give an approximate minimum detection of 40 ppb.

Output from the GC/EC was measured by a Hewlett Packard 3390A integrator, which was programmed to integrate peak areas, recognize referenced peaks, and quantify all unrecognized peak areas in terms of CCl_4 equivalents. Printout was given in units of ppb.

3.2.1.4 External Standards For Qualification--

External standards used to quantify the POHC's in the gas samples were generated using dynamic gas standards. Permeation tubes and diffusion tubes provide dynamically prepared standards for a large number of solvents. Since the permeation and/or diffusion tubes are post-calibrated gravimetrically by weight loss, the permeation and/or diffusion rate and thus that gas standard developed can be traceable to National Bureau of Standards. Another advantage is that multiple standards can be prepared in the same flowing stream, similar to the gas sample to be analyzed.

By using a dynamic standards system, the material that is permeated/diffused is in equilibrium with the environment in which it is moving. Therefore, there is no sample loss due to absorption on the walls of the system. The use of gas standards supplied in a cylinder (not available for the designated POHC's in the ppm to ppb range) means that these cylinder standards are secondary standards which have been calibrated by either infrared or GC techniques.

Two basic systems are needed to attain the high level of accuracy capable with permeation and/or diffusion tubes for the preparation of dynamic gas standards. The first is a temperature-controlled chamber system such that the tube can be held at a known temperature within ± 0.1°C. The second system must provide for a flow of diluent air to mix with the permeant/diffusant from the tube, and this flow must be stable and capable of being read to ±1% accuracy. It should also be variable over a range of different flows to provide known variation in the concentration of the dynamic gas standard, i.e., multiple calibration points.

The system used at San Juan Cement demonstration burn was a pair of AID Model 320A Calibration Systems, as shown in the flow schematic in Figure 3-9. A description of the flow system follows.

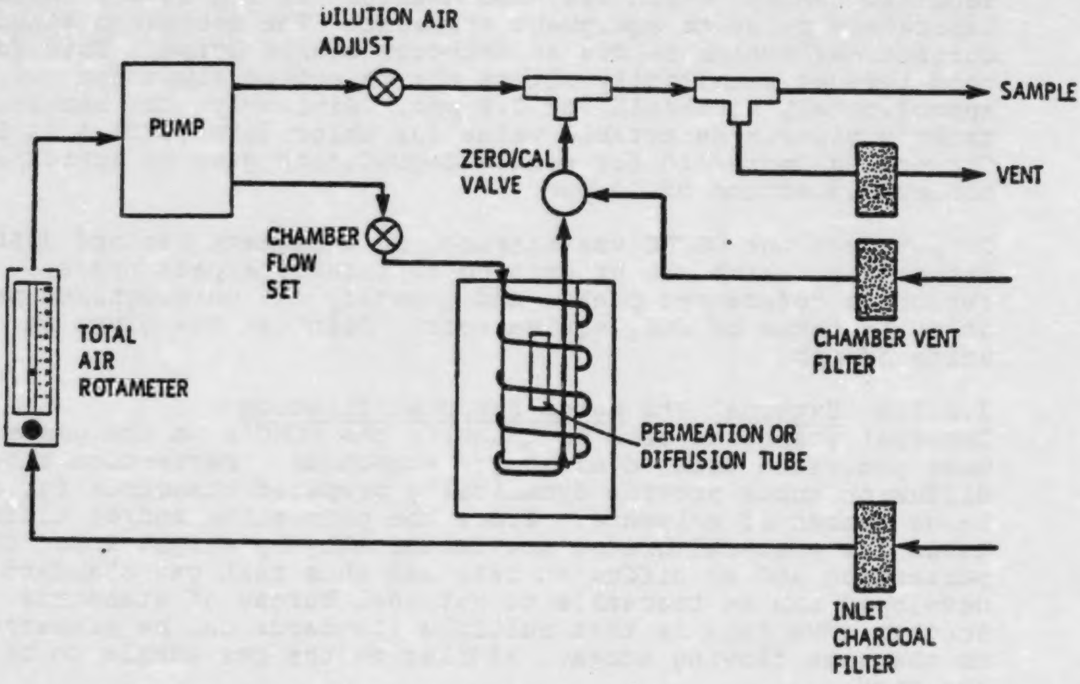

DILUTION AIR ADJUST
PUMP
SAMPLE
ZERO/CAL VALVE
VENT
CHAMBER FLOW SET
TOTAL AIR ROTAMETER
CHAMBER VENT FILTER
PERMEATION OR DIFFUSION TUBE
INLET CHARCOAL FILTER

Figure 3-9. Flow schematic of AID 320A gas calibration system.

Ambient air is drawn into the Model 320A through the particulate/charcoal filter (rear panel) by the pump. This filter removes all particulates as well as virtually all of the commonly used permeants. The "zero air" is then drawn through a two ball flow meter for accurate total air flow measurement. The top ball (glass) is used for low flows between 300 and 700 ml/min. The bottom ball (stainless steel) is used for the high flow range from 700 to 1500 ml/min. Specific calibration curves are provided for each ball in each Model 320A. They are individually calibrated to ±1% accuracy prior to leaving the factory. They were also calibrated in the field using a 10cc and 100cc soap bubble flowmeter.

The pump is a two headed pump and splits the incoming "zero air" into two separate flow streams, a fixed low flow for the chamber flow and an adjustable flow for the dilution flow. Power to the pump is dc.

The diluent air flow leaves the pump and passes through a needle valve accessable on the front panel as the DILUTION AIR ADJUST. This valve is used to change the amount of dilution air desired within the range of 300 and 1500 ml/min. The dilution air leaves the needle valve and passes to the mixing "T" where it is mixed with the tube air flow.

The tube air flow leaves the other side of the pump and passes through a factory set needle valve located inside the instrument. This valve is used as a fixed restriction to adjust the tube air flow to a low value. This flow is constant through the tube oven under all operating conditions. The tube air then enters the oven where it passes through a long coil of copper tubing surrounding the oven chamber. This permits the tube flow to fully equilibrate to oven temperature before passing into the permeation tube chamber itself.

The tube flow enters the permeation chamber through the glass frit sealed into the bottom of the chamber. It then passes across the permeation tube itself contained inside the chamber. A sensing thermistor supplies a signal to the termperature readout circuit thus giving the temperature of the gas and permeation tube at this point. Controller stability is within ±0.025°C of set temperature. The tube air flow plus the permeant then leaves the oven through the Teflon fitting sealing the top of the permeation chamber and the Teflon tube. All material of construction from the permeation chamber on that the permeant may contact is Teflon.

The tube flow (plus permeant) then passes to a solenoid valve. This valve is controlled from the front panel and is labeled FLOW SELECT. In the ZERO AIR position the entire tube air flow is directed to a charcoal filter and the vented. In this position none of the permeant is mixed with the dilution air and only "zero" dilution air is supplied to the SAMPLE port at the rear of the instrument.

When the valve is in the CALIBRATE position the entire tube air flow plus permeant is directed through the valve to the mixing "T" where it is mixed with the diluent air. The mixed diluent and tube air flows are then directed to another "T". One side of this "T" is vented to atmosphere through the rear and is labeled DUMP. The other exit of the "T" is also available on the rear panel at the SAMPLE port and provides the calibrating gas at atmospheric pressure for the sampling system of the GC instrument to be calibrated.

The entire GC/standard generation system used is depicted schematically in Figure 3-10 and pictorially in Figure 3-11. Permeation tubes containing methylene chloride and chloroform were obtained from AID and were placed together in one AID calibrator. A diffusion tube containing carbon tetrachloride was placed in a second AID Calibrator. Three separate flowrates were marked on each Calibrator so that three gas standards in the ppb range could be generated for each POHC contained in the permeation/diffusion tube.

3.4.1.4.1 Permeation and diffusion tube theory -- Permeation tubes have been described and used for over fifteen years to generate gas mixtures dynamically that are of primary standard quality [13]. The tubes are generally made by sealing liquids into small diameter (3.2-9.5 mm) FEP Teflon tubes of varying lengths. In most cases the chemical placed in the tube is a gas at room temperature, but it is held under its saturation vapor pressure as a liquid in the tube. After an initial induction period of 3-10 days (more in some cases), the material permeates uniformly through the Teflon wall of the tube. The tube can be accurately calibrated by measuring its weight loss over a period of days at constant temperature.

With a given material the rate will be proportional to the area of the tube (controlled mostly by length), inversely proportional to the thickness of the wall, and finally proportional to the vapor pressure differential across the wall of the tube. The vapor pressure outside the tube is very low (essentially zero) since in use gas mixtures are in the range of parts-per-million concentration. Thus the saturation vapor pressure inside the tube determines the rate for a given chemical in a given fixed dimension tube. This pressure is a rather marked function of the temperature of the permeation tube (actually the liquid in the tube). Thus for a given tube the rate varies with temperature. Empirically the relationship of permeation rate and

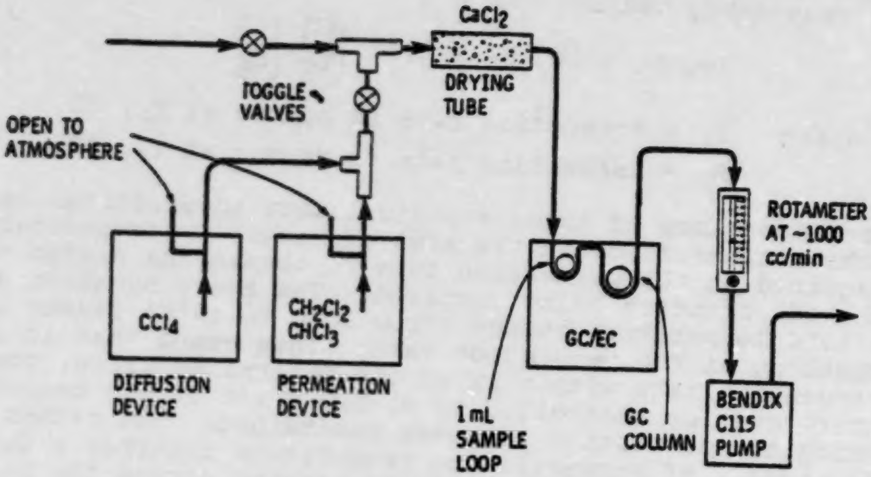
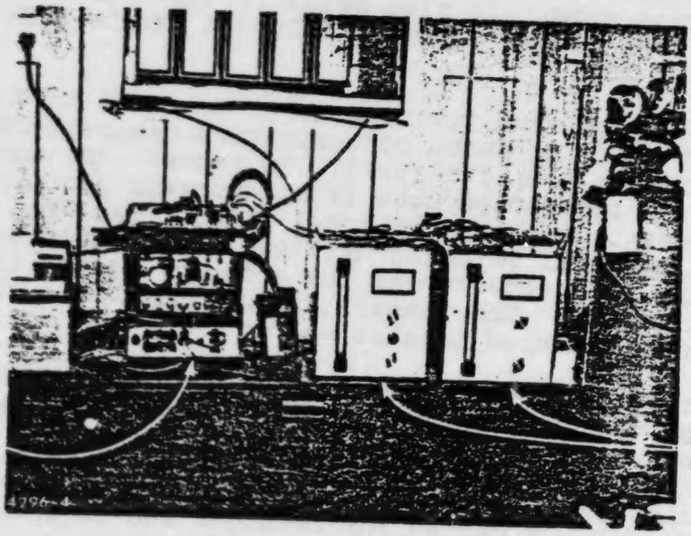

CaCl2
TOGGLE VALVES
DRYING TUBE
OPEN TO ATMOSPHERE
ROTAMETER AT ~1000 cc/min
CCl4
CH2Cl2
CHCl3
GC/EC
DIFFUSION DEVICE
PERMEATION DEVICE
1 mL SAMPLE LOOP
GC COLUMN
BENDIX C115 PUMP

Figure 3-10. Schematic diagram of GC/dynamic gas generation system.



GC/EC

Dyanamic Calibrators

Figure 3-11. Pictorial diagram of GC/EC measurement system in laboratory trailer.

temperature has been found to correspond to a typical vapor pressure - temperature relationship. Over reasonable temperature that permeation tubes can be used, the following equation is reasonably valid:

$$\log R_1 = \log R_2 - 2950 \left[\frac{1}{T_1}\right] - \left[\frac{1}{T_2}\right] \qquad (8)$$

where R_1 = Permeation rate in ng/min at T_1, °K.

R_2 = Permeation rate in ng/min at T_2, °K.

The importance of these empirical data in practical use of permeation tubes comes in the area of necessary temperature control required on the permeation tube to obtain the needed accuracy of the gas standard being prepared. The above equation states that a 10°C temperature change (from 30°C to 40°C) causes a virtual doubling of the permeation rate. This means that to insure a permeation rate within 1% of the determined value, the temperature must be controlled to within 0.1°C of the temperature at which the permeation rate was determined. The rather strong dependence of permeation on temperature requires a further consideration. The flow of gas passing across the permeation tube must be equilibrated to the temperatures of tube before it passes across the tube. Without this equilibration the gas will alter the temperature of the tube in an unknown fashion thus affecting the permeation rate and the concentration in an unknown fashion. A volume of excellent thermal exchange at the controlled temperature must be provided in the gas stream ahead of the permeation tube. It also helps if this gas flow is kept constant and at a low flow. Further dilution can be done after the permeation chamber.

Generally the need for permeation tubes is in the preparation of a standard of known concentration generally expressed as parts-per-million (vol/vol). To convert the output or permeation rate of a permeation tube from nanograms per minute into ppm it is necessary to know the total flow of gas with which the permeating material is being diluted. This gas flow must be known with the same accuracy as the accuracy needed in the final concentration. The temperature at which this volumetric flow of gas is measured is also needed.

To get ppm (vol/vol) the material permeated through the tube must be converted from a weight per unit time to a volume of gas per unit time. Since permeation rates are usually reported in nanograms per minute (ng = 10^{-9} g) volume can be obtained by dividing by the density of the gas or by multiplying by a constant, K. K varies for each gas and is either taken from tables or is calculated as follows:

$$K\ (\mathrm{nl/ng}) = \frac{22.4}{MW} \times \frac{273 + T}{273} \times \frac{760}{P} \qquad (9)$$

where MW = Molecular weight of the permeating gas
T = Temperatures in °C
P = Absolute pressure in mm Hg

(N.B.: T and P are the temperature and pressure at which the volumetric flow of matrix gas is measured, not necessarily the temperature and pressure at which the permeation tube is being held.) This equation for K can be simplifid for most applications by assuming a temperature of 25°C and 760 mm Hg pressure. Then

$$K = \frac{24.45}{MW} \qquad (10)$$

These are the conditions that are normally used to provide K values in tables. Note that temperature can vary by 3°C on either side of 25°C or pressure can vary by almost 8 mm Hg and still maintain 1% accuracy in K. For conditions beyond this K must be corrected to maintain 1% accuracy.

Division of the ml/min of permeant by the volumetric flow of matrix gas gives the concentration of permeant in the matrix gas. Thus:

$$C = \frac{R \times K}{F} \qquad (11)$$

where C = Concentration in ppm (vol/vol)
R = Permeation rate in ng/min
K = Constant for specific permeant
F = Total matrix gas flow in ml/min.

If current "best practice" is followed of using a low flow rate of matrix gas across the permeation tube followed by a major dilution after the permeation chamber both flows must be added and used as F in the above equation. The flow meter in the Model 320A measures the combined flow thus giving the value to be used directly. The actual chamber flow need not be known accurately to produce accurate standards.

The diffusion tube is a liquid filled reservoir with a long neck of precision bore glass tubing. Material is placed in the reservoir of the diffusion tube. If the diffusion tube is then held at constant temperature, the material diffuses through the precision bore capillary neck of the diffusion tube at a constant rate following thermal equilibration. The amount of material that diffuses per unit time is determined by weight loss on the diffusion tube itself. Certainly theory can predict the diffusion rates with reasonable accuracy, but for calibration purposes, weight loss is the technique used to measure the diffusion rate.

If while the diffusion tube is being thermostatted, a known flow of air passes across the diffusion tube, the concentration of the material in the air can be calculated. This then provides a known dynamic standard for that particular material in air. Diffusion tubes come in three different bore sizes: 0.5 mm, 2mm, and 5 mm. The liquid reservoir of the diffusion tube can accommodate about three ml of the material. The length of the reservoir is approximately 4 to 5 cm. Standard tubes are supplied with a capillary neck of approximately 12 to 13 cm. The necks can be shortened to any desired length simply by using a file and standard glass tube cutting techniques.

The fundamental equation used not only to size diffusion tubes but also to calculate the concentration obtained in the flowing gas stream is Equation (11), identical to that used for permeation tubes.

The basic theory of diffusion tubes at it relates to the dynamic generation of known standards has been known for over 20 years [14]. The theoretical equation describing the diffusion rate from these tubes is:

$$R = 2.216 \times 10^6 \frac{DMPA}{TL} \log \frac{P}{P-p} \qquad (12)$$

where R = Diffusion rate, ng/min

D = Diffusion coefficient at T & P, cm^2/sec

M = Molecular weight

P = Total pressure, torr Hg

A = Cross sectional area diffusion path, cm^2

T = Temperature, °K

L = Length of diffusion path, cm

p = partial pressure of sample at T, torr Hg

The diffusion coefficient is also a temperature and pressure dependent term as follows:

$$D = D_o \left(\frac{T}{T_o}\right)^m \left(\frac{P_o}{P}\right) \qquad (13)$$

where D_o = Diffusion coefficient at the standard conditions of T_o = 273°K and P_o = 760 torr Hg.

m = constant - usually 2 but may be 1.75

If the above two equations are combined and the values of T_o and P_o placed in the numerical constant the following equation results:

$$R = 6.169 \times 10^6 \, D_oM \left(\frac{A}{L}\right)\left(\frac{T}{T_o}\right)^{m-1} \log \frac{P}{P-p} \tag{14}$$

where

D_oM = Sample constant

$\frac{A}{L}$ = Diffusion path geometry

$\left(\frac{T}{T_o}\right)^{m-1} \log \frac{p}{P-p}$ = Conditions of diffusion

The importance of temperature control can be approximated by assuming an average of about 50% change of vapor pressure for a 10°C temperature change (a reasonable average for organic materials). This will cause an approximate change in the log term of 50%. The 10°C change will cause approximately a 3% change in the temperature term in the same direction. Overall, then, a 1°C change causes about a 5% change in diffusion rate. Temperature should be controlled to within 0.2°C to maintain 1% accuracy in the developed standard.

3.4.1.4.2 -- Example calculation of gas standards--Using the soap bubble flowmeters for flow calibration, with several digitally timed flow rate runs used for each rotameter flow setting on the Calibrator, flow rates measured and calibrated were:

1000 cm^3/min, 647 cm^3/min, 421 cm^3/min

The value for K in Equation (11) for chloroform is:

$$K = \frac{24.45}{MW}$$

where MW = 119.83

K = 0.204

The calculated permeation rate of chloroform in permeation tube no. 8806, as certified by the supplier, was 545 ng/min. Substitution into Equation (12) for each flowrate gives:

$$C = \frac{RxK}{F}$$

$$C_1 = \frac{(545)\ (0.204)}{(1000)} = 0.1112 \text{ ppm or } 111 \text{ ppb}$$

$$C_2 = \frac{(545)\ (0.204)}{(647)} = 0.1718 \text{ ppm or } 172 \text{ ppb}$$

$$C_3 = \frac{(454)\ (0.204)}{(421)} = 0.2641 \text{ ppm or } 264 \text{ ppb}$$

These flow rates thus gave a three point calibration curve. Post-calibration of the gas standards was done by gravimetric determination of the permeation tube on an electronic balance pre-calibrated with Class S weights (see Section 9). The comparison of measured to calculated permeation/diffusion rate is in Table 3-3. By substituting the gravimetrically determined value of 671 ng/min into Equation (12), the calibration curve used for post-test data reduction of CG/EC results is given by 137 ppb, 212 ppb, and 325 ppb.

TABLE 3-3. POST-TEST GRAVIMETRIC CALIBRATION FOR DYNAMIC GAS POHC STANDARDS

	Time in		Time out		Total time, hr	Initial weight, gm	Final weight, gm.	Net loss, gm	Actual permeation rate,[a] ng/min	Theoretical or certified permeation rate,[b] ng/min	Error, percent relative
	hr	date	hr	date							
Permeation tube no. 8805 (CH_2Cl_2)	1030	10/20/81	2140	2/12/82	2,723.17	4.3179	4.1495	0.1684	1,031	2,810	+173
Permeation tube no. 8806 ($CHCl_3$)	1030	10/20/81	2140	2/12/82	2,723.17	4.7313	4.6216	0.1097	671	545	-18.8
Diffusion tube (CCl_4)	1030	10/20/81	2140	2/12/82	2,723.17	13.4187	13.0109	0.4178	2,557	2,560	+0.12

[a] Measured by weight loss over extended period of time.

[b] Calculated by diffusion equation, or certified by permeation tube supplier.

3.4.2 Particulate Matter

The procedure and equipment used for quantitative particulate collection met the specifications outlined in Method 5 of the Federal Register [15]. The flue gas exhaust stack was traversed for 48 points at 2 minutes/point for representative sample collection. Mass emissions were collected over a period of 2 to 3 hours from approximately 1.27 to 1.70 m^3 (45 to 60 scf) of exhaust gas.

The front half of the Method 5 train (filter and probe rinse) was used to determine particulate loading; no pre-cyclone was used in front of the filter due to light loadings.

The filters used were 82 mm Gelmon fiberglass filters. The probe was a heated 3.05 m glass-lined probe. Method 5 analysis was performed at the MRC Dayton Laboratory.

3.4.3 Sulfur Dioxide

Sulfur dioxide was collected employing EPA Method 6, Option 2 as outlined in the Federal Register [16]. In this method the back half of the Method 5 particulate sampling train is used for Greenberg-Smith impinger collection of 1.27 to 1.70 m^3 (45-60 scf) of gas rather the duplicate midget impinger runs of 0.014 m^3 (0.5 scf) of gas. Analysis of the sample then follows the EPA Method 8 titration procedure.

3.4.4 Nitrogen Oxides

EPA Method 7 was employed, as specified in the Federal Register [17], to determine emissions of nitrogen oxides. This grab-sample technique was repreated four times during the collection of particulate samples.

3.4.5 Carbon Dioxide and Oxygen

CO_2 and O_2 were determined for stack-gas molecular weight determination. An integrated sample from the Method 5 console exhaust was collected in a Tedlar gas sample bag and analyzed using EPA Method 3 as specified in the Federal Register [18]. Fyrite analyzers were used, which employ the well-known "Orsat" method of volumetric measurement involving chemical absorption of the gas sample by a chemical absorbent.

3.4.6 Visible Emissions

A certified smoke reader was present at the site during every testing day. The plume from Kiln #2 was monitored during each burn and readings were recorded once each month to ensure that the plant remained in compliance with regulations (less than 20% opacity average). Visible emissions were read by EPA Method 9 as outlined in the Federal Register [19].

3.4.7 Total Hydrocarbons (THC)

Low molecular weight total gaseous hydrocarbons (C_1 - C_5) were measured continuously during baseline and waste burn testing. A Beckman Model 402 hydrocarbon analyzer was used, consisting basically of a flame ionization detector (FID) coupled to a strip chart recorder. Gas introduction to the analyzer was kept at 175°C by heated lines. Calibration gases of zero gas, 3, and 44 ppm CH_4 in air were used as span gases. Data reduction was by 15-min averages because emission levels were always smooth.

3.4.8 Carbon Monoxide (CO)

CO emissions were monitored continuously by employing EPA Method 10 with a Beckman 864 nondispersive infrared analyzer [20]. Calibration gases of zero air, 310, 605, and 897 ppm CO in nitrogen were used as span gases. This method was very troublesome and labor intensive on a wet process cement kiln because of the high levels of moisture (30%) and CO_2 (17%) present in the stack gas. Each of these must be removed from the sample gas stream because they are a positive interference in NDIR analysis.

3.4.9 Source Assessment Sampling System (SASS)

The SASS train was used to collect enough sample to identify products of incomplete combustion, perform organic compound speciation, and lower detection limits for dioxin and furan analyses. The SASS method was developed as a screening tool for EPA Level 1 sampling and analysis, wherein large quantities of stack gas are collected (10-30 m^3) so that particulate, organic, and inorganic classes of compounds could be identified. In this program the collection and identification of only organic materials was the primary utility of the SASS train.

Accordingly, the SASS train was modified to focus on organic compound collection, as shown schematically in Figure 3-12.

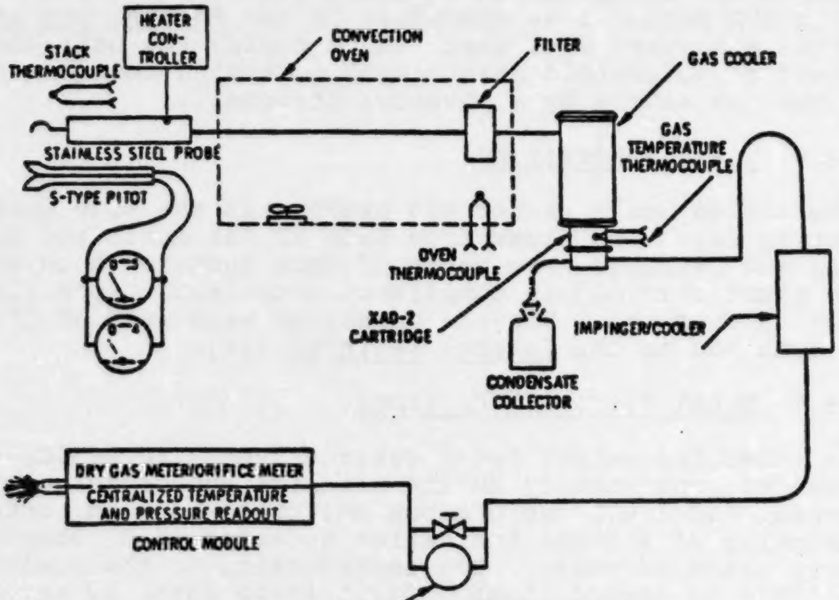

HEATER CON-TROLLER
STACK THERMOCOUPLE
CONVECTION OVEN
FILTER
GAS COOLER
STAINLESS STEEL PROBE
GAS TEMPERATURE THERMOCOUPLE
S-TYPE PITOT
OVEN THERMOCOUPLE
XAD-2 CARTRIDGE
IMPINGER/COOLER
CONDENSATE COLLECTOR
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10-CFM VACUUM PUMP (2)

Figure 3-12. Schematic of modified Source Assessment sampling system.

The modified SASS train consisted of a stainless steel probe, a heated oven module containing the filter (no cyclones for particle sizing), a solid sorbent (XAD-2) trap with condensate collector, and a system for flow measurement and pumping. An impinger containing 750 g of 3 to 8 mesh color-indicating silica gel was placed before the pump to prevent moisture from reaching the pump. The standard SASS train impinger collection system for trace metals (inorganics) was replaced by water-containing impingers.

Semivolatile organic material was collected in a cartridge containing XAD-2 sorbent resin with the capability of absorbing a broad range of organic species. The ~130g XAD-2 cartridge in the SASS train is sized to ensure efficient collection of vapor phase organic materials with boiling points $\geq$100°C for a 30 m^3 stack gas sample. The organic collector module follows the oven unit and is comprised of four primary components: the gas cooler, the sorbent trap, the aqueous condensate collector, and a temperature controller, as shown in Figure 3-13.

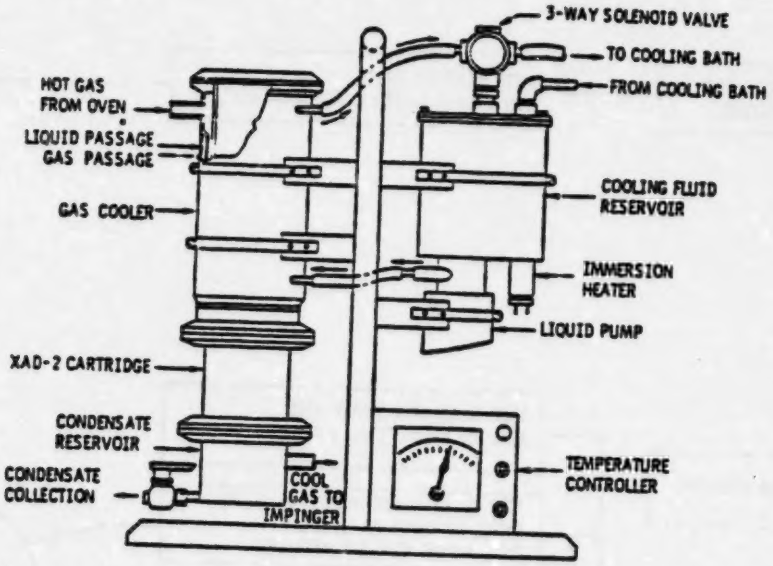

3-WAY SOLENOID VALVE
TO COOLING BATH
FROM COOLING BATH
HOT GAS FROM OVEN
LIQUID PASSAGE
GAS PASSAGE
GAS COOLER
COOLING FLUID RESERVOIR
IMMERSION HEATER
LIQUID PUMP
XAD-2 CARTRIDGE
CONDENSATE RESERVOIR
CONDENSATE COLLECTION
COOL GAS TO IMPINGER
TEMPERATURE CONTROLLER

Figure 3-13. XAD-2 sorbent trap module.

At the site, the train was assembled, and the oven was heated to 205°C (400°F) before each run. The resin trap was maintained at 20°C (68°F) during the run. A leak check was made before the start of each run; a leak rate of less than 23.6 x 10^{-6} m^3/s at 67.7 kPa (0.05 cfm at 20 in. Hg) was considered acceptable.

The SASS train was not designed for traversing a stack. From previous velocity traverses a position near the center of the stack was located which has an average stream velocity. The velocity at the sampling point, the stack temperature, and moisture content were used to calculate the size of the probe nozzle which gave approximately isokinetic sampling.

Gas volumes collected ranged from 8.5 to 18.4 m^3 over periods from 200 to 300 min. The bulk of the organic compounds of interest should be trapped in the sorbent resin; however, the particulate filter, tubing rinses, organic module rinses, and condensed water also provided samples for analysis.

At the completion of a sampling run, the resin trap was removed and capped. The entire train, from probe tip to filter holder to gas cooler was cleaned with methylene chloride and the sample bottled in amber glass. Cooler trap contents were measured, and the liquid poured into an amber bottle. The silica gel impinger contents were weighed, and the material discarded. All samples were stored in a refrigerator on site and delivered on ice to MRC's Dayton Laboratory. Figures 3-14 and 3-15 illustrate the cleanup and sample handling procedures.

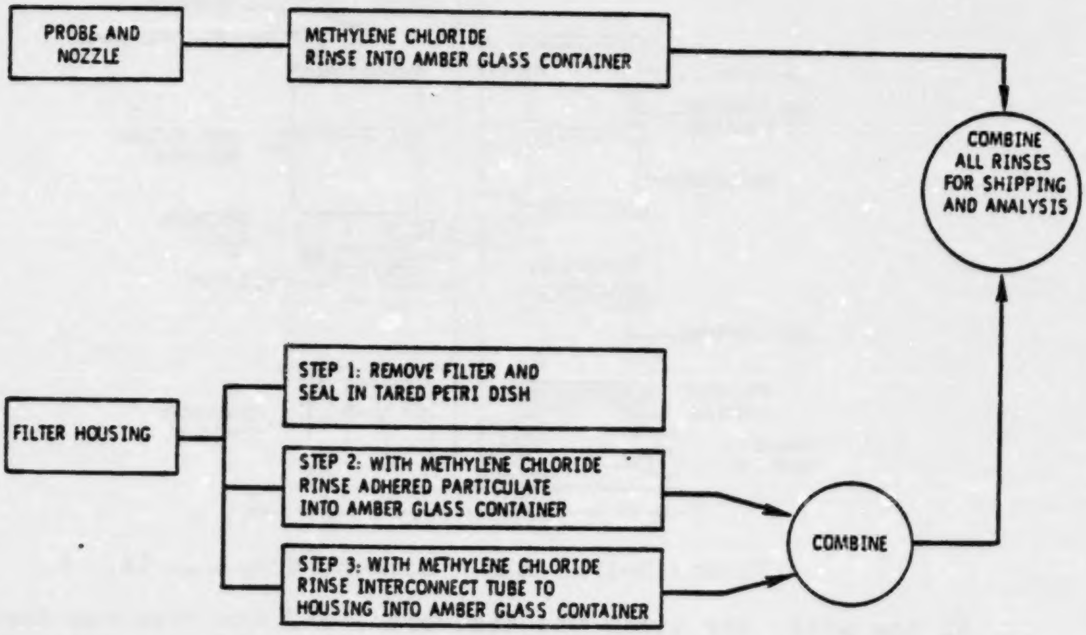

PROBE AND NOZZLE
METHYLENE CHLORIDE RINSE INTO AMBER GLASS CONTAINER
COMBINE ALL RINSES FOR SHIPPING AND ANALYSIS
FILTER HOUSING
STEP 1: REMOVE FILTER AND SEAL IN TARED PETRI DISH
STEP 2: WITH METHYLENE CHLORIDE RINSE ADHERED PARTICULATE INTO AMBER GLASS CONTAINER
STEP 3: WITH METHYLENE CHLORIDE RINSE INTERCONNECT TUBE TO HOUSING INTO AMBER GLASS CONTAINER
COMBINE

Figure 3-14. Sampling handling and transfer - SASS train nozzle, probe, and filter.

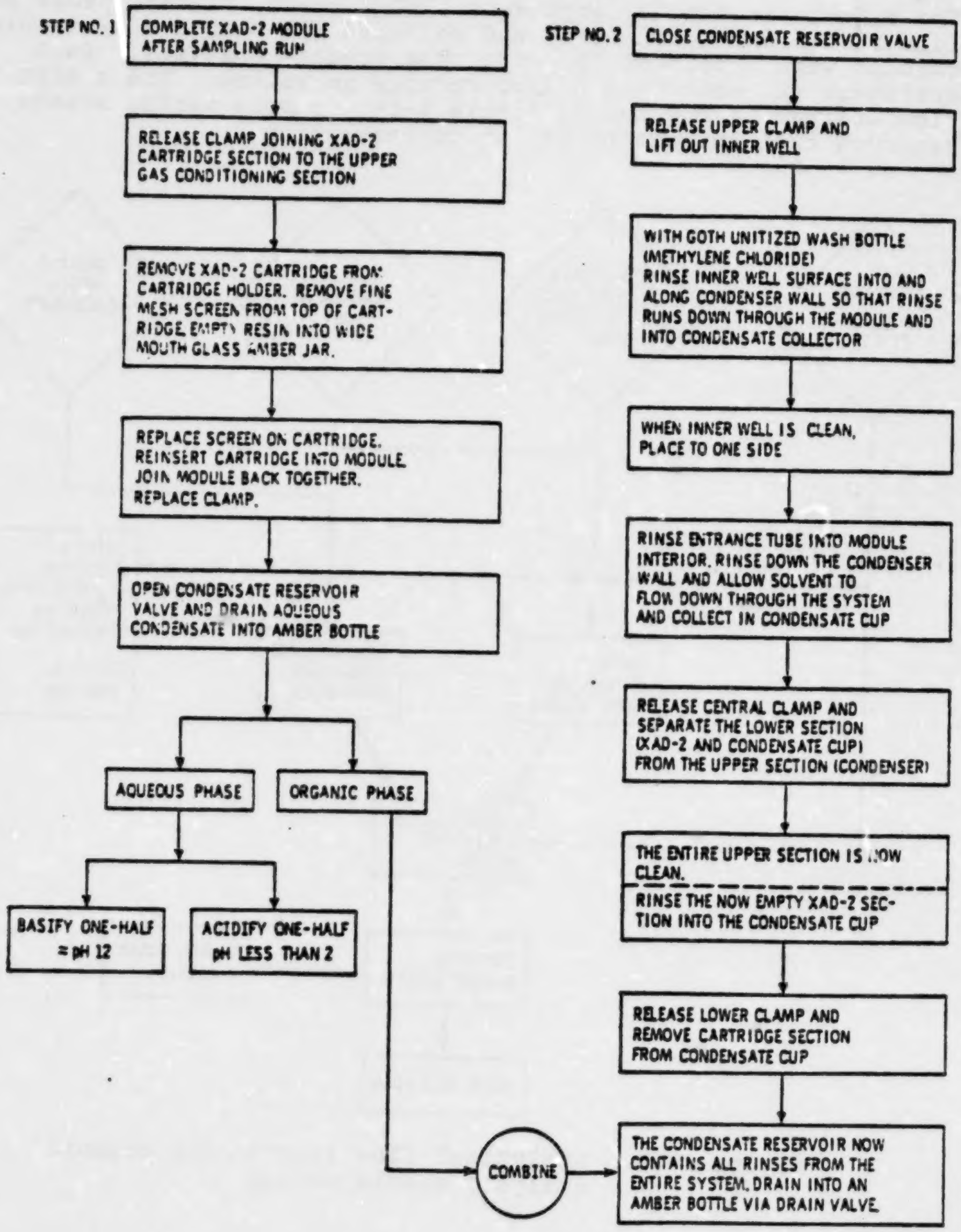

STEP NO. 1
COMPLETE XAD-2 MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING XAD-2 CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE XAD-2 CARTRIDGE FROM CARTRIDGE HOLDER. REMOVE FINE MESH SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO WIDE MOUTH GLASS AMBER JAR.
REPLACE SCREEN ON CARTRIDGE. REINSERT CARTRIDGE INTO MODULE. JOIN MODULE BACK TOGETHER. REPLACE CLAMP.
OPEN CONDENSATE RESERVOIR VALVE AND DRAIN AQUEOUS CONDENSATE INTO AMBER BOTTLE
AQUEOUS PHASE
ORGANIC PHASE
BASIFY ONE-HALF ≈ pH 12
ACIDIFY ONE-HALF pH LESS THAN 2
STEP NO. 2
CLOSE CONDENSATE RESERVOIR VALVE
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
WITH GOTH UNITIZED WASH BOTTLE (METHYLENE CHLORIDE) RINSE INNER WELL SURFACE INTO AND ALONG CONDENSER WALL SO THAT RINSE RUNS DOWN THROUGH THE MODULE AND INTO CONDENSATE COLLECTOR
WHEN INNER WELL IS CLEAN, PLACE TO ONE SIDE
RINSE ENTRANCE TUBE INTO MODULE INTERIOR. RINSE DOWN THE CONDENSER WALL AND ALLOW SOLVENT TO FLOW DOWN THROUGH THE SYSTEM AND COLLECT IN CONDENSATE CUP
RELEASE CENTRAL CLAMP AND SEPARATE THE LOWER SECTION (XAD-2 AND CONDENSATE CUP) FROM THE UPPER SECTION (CONDENSER)
THE ENTIRE UPPER SECTION IS NOW CLEAN.
RINSE THE NOW EMPTY XAD-2 SECTION INTO THE CONDENSATE CUP
RELEASE LOWER CLAMP AND REMOVE CARTRIDGE SECTION FROM CONDENSATE CUP
COMBINE
THE CONDENSATE RESERVOIR NOW CONTAINS ALL RINSES FROM THE ENTIRE SYSTEM. DRAIN INTO AN AMBER BOTTLE VIA DRAIN VALVE.

Figure 3-15. Sample handling and transfer - XAD-2 module.

3.4.10 Organic Species Analysis

The SASS train sample components (XAD-2 resin, filter, probe and line rinse, and condensate) and selected EPA Method 5 particulate catches were submitted for wide scan organic analysis. Each component was extracted and/or reduced in volume. The analytical flow diagrams are shown in Figure 3-16. Sample workup sheets recorded each extraction and/or concentration.

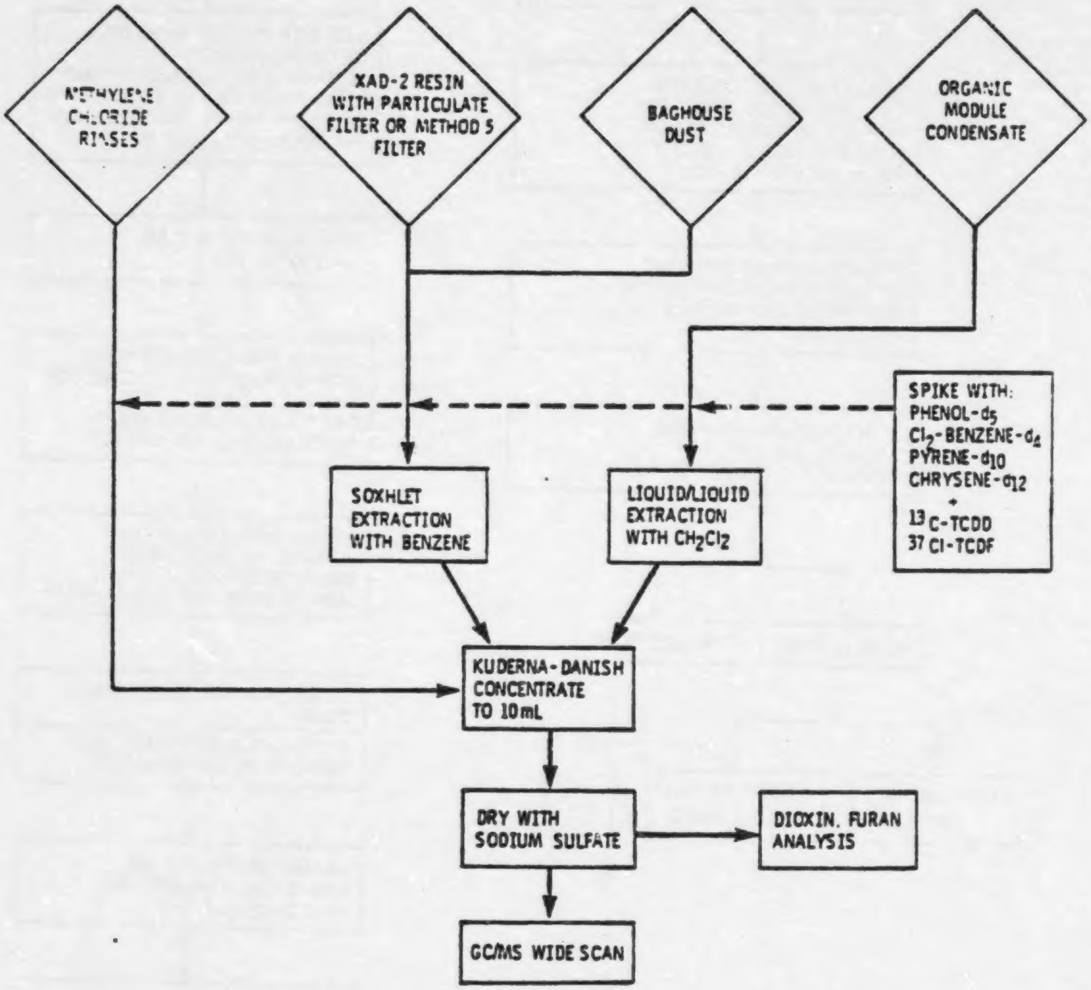

METHYLENE CHLORIDE RINSES
XAD-2 RESIN WITH PARTICULATE FILTER OR METHOD 5 FILTER
BAGHOUSE DUST
ORGANIC MODULE CONDENSATE
SPIKE WITH:
PHENOL-d5
Cl2-BENZENE-d4
PYRENE-d10
CHRYSENE-d12
+
13C-TCDD
37Cl-TCDF
SOXHLET EXTRACTION WITH BENZENE
LIQUID/LIQUID EXTRACTION WITH CH2Cl2
KUDERNA-DANISH CONCENTRATE TO 10mL
DRY WITH SODIUM SULFATE
DIOXIN, FURAN ANALYSIS
GC/MS WIDE SCAN

Figure 3-16. Analytical flow diagram for organic analysis sample workup.

The GC/MS analyses were performed by automated capillary column chromatograph using a Hewlett-Packard 5985-A GC/MS with a 5934 data system, which used Revision C Software and included a 7920 multi-drive disc unit. Since the peaks obtained in capillary column GC/MS analysis are only a few seconds wide (much narrower than packed-column peaks), it is necessary to scan the mass spectrometer at its maximum rate to generate reliable mass spectra -- approximately 4500 spectra for a 40-minute run, depending on the initial MS scan delay, as compared to perhaps 700 for a 40-minute, packed-column run. A low detection threshold must also be used to capture the information contained in small peaks, which combines with the large number of spectra to consume enormous amounts of computer disc space in a given analysis. In some cases several GC/MS analyses could fill a data disc cartridge. Thus, to perform a series of 10 to 20 analyses, using the automatic injector system, requires the use of several discs for data acquisition. This is only possible in an automated mode on the Hewlett-Packard system by using the multidisc drive in which the equivalent of up to 19 discs could be accessed simultaneously.

The relevant GC/MS parameters used for the analyses are summarized below:

- 30 m fused silica SE-54 WCOT column
- Column head pressure, 7-9 psi
- MS operating pressure, 1 x 10^5 to 4 x 10^6 torr
- Septem purge on a 0.5 min
- Initial temperature, 50°C
- Initial temperature held for 4 minutes
- Heating rate, 8°C/min
- Final temperature, 300°C.
- Total analysis time, 40 min
- Injector, spitless mode, temperature, 250°C
- Transfer line temperature, 250°C (fused silica column through this zone, directly to the MS source)
- Electron energy, 70eV
- A/D rate, 1 measurement/0.125 amu; scan rate, approximately 0.6 s/scan
- Mass spectrometer scan delay, 3.0 min

The routine procedure used for GC/MS analysis was to transfer 150 µL of the sample extract into 1.5 mL sample vials along with 150 µL of a 100 µg/mL anthracene-d_{10} in methylene chloride internal standard. The vial was capped and placed in the autosampler, which injected approximately 1 µL into the GC, operating in the splitless mode.

The following protocol was followed in interpreting the mass spectral data obtained from San Juan extracts:

1) Spectra of compounds detected as peaks in the Hewlett-Packard BATCH program with a 1% to 5% threshold (depending upon the complexity of the sample) were automatically compared with standard spectra in the computerized EPA/NIH mass spectral data base using the Probability Based Search (PBS) software supplied by Hewlett-Packard. A goodness of fit parameter was generated (1.0 being a perfect match) for the ten matches closest to 1.0.

2) The results from these searches were reviewed by an experienced mass spectroscopist using the Hewlett-Packard supplied spectral comparison software, SPDIF, to compare the sample spectra with the standard spectra identified by the SEARCH program.

3) In cases where the spectral agreement was judged to be adequate, compound identities were assigned. When compound isomers produced similar spectra, no specific isomer could be identified based solely upon mass spectral data.

4) In cases where the agreement was not adequate, identifications were made on the basis of manual interpretation (when obvious), or compounds were listed as unknown with their major masses given in parentheses. If a high even mass was present with odd fragment masses, the even mass was underlined to indicate a possible molecular ion.

The approach outlined above was adopted to minimize the cost and time required for the analyses of large amounts of capillary chromatographic mass spectra by maximizing the use of computerized data interpretation techniques.

These comparative mass spectral plots were reviewed by an expert mass spectroscopist who, based on experience in mass spectrometry and mass spectral interpretation, accepted or rejected the computer-generated identification.

Some considerations that go into making decisions on the identity of components in sample extracts include:

1) Unknown spectrum contains all peaks with intensities greater than 10% of the base peak in the standard spectrum.

2) All mass intensities of multiplets present in the standard spectrum must also be present in the unknown spectrum with similar relative intensities.

3) If peaks are present additional to those in the standard spectrum of a compound, then it is assumed that the additional peaks are due to the presence of an unknown co-eluting compound. In obvious cases of mixed spectra, the PBS

SEARCH program identified the presence of a mixture of spectra with a "+" in the column following the match factor. Where mixed spectra are confirmed using the spectral comparison program, the major identified compound was listed along with an estimate of the percent of the unknown compound present in the mixed spectrum.

The good chromatography generally observed in most extract analyses resulted in relatively pure mass spectra being obtained for most compounds.

The calculations used for determining the concentration of organics in sample extracts were performed in two ways. All levels of deuterated spiking compounds were determined using the FID response of each of the compounds, relative to the anthracene-d_{10} response. Therefore, all recovery data were calculated using authentic standards.

The amounts of all other compounds were determined assuming the total ion response of each compound to be equal to the response of the anthracene-d_{10} internal standard. This latter calculation was made using the following relationship:

$$\text{Concentration of X} = (1000\ \mu g)\ \frac{\text{Total ion area X in unknown}}{\text{Total ion area anthracene-}d_{10}}$$

3.4.11 Dioxin and Furan Analysis

Analysis for the presence of polychlorinated dibenzodioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) was conducted on the SASS train components, selected Method 5 particulate samples, and RCRA EP extracts of baghouse dusts. The analytical flow diagram for sample workup is shown in Figure 3-17.

After the concentrated extract has had a base wash to remove phenols and a water wash, the concentrated extract was then applied to a chromatography column packed with 4 grams of Woelm Basic alumina which had been conditioned at 550°C for 12 hours and topped with 1 gram of anhydrous sodium sulfate. The concentrate was applied to the column and the column eluted with 10 mL of 2% CH_2Cl_2/hexane and this fraction saved. 100 µL of n-dodecane keeper was then added to this fraction and the sample concentrated to 100 µL after repeated CH_2Cl_2 rinses of the walls of the collection tube.

The extract was analyzed on a Hewlett Packard 5985B GC/MS system using a 50 m Silar 10C capillary column for the separation. The mass spectrometer was operated in the selected ion monitoring mode following m/z 257 (COCl loss from TCDD), M/z 320 (molecular ion for TCDD), m/z 322 (molecular ion for TCDD) and m/z 334 on the relative response of the native (unlabeled) TCDD to the labeled internal standard.

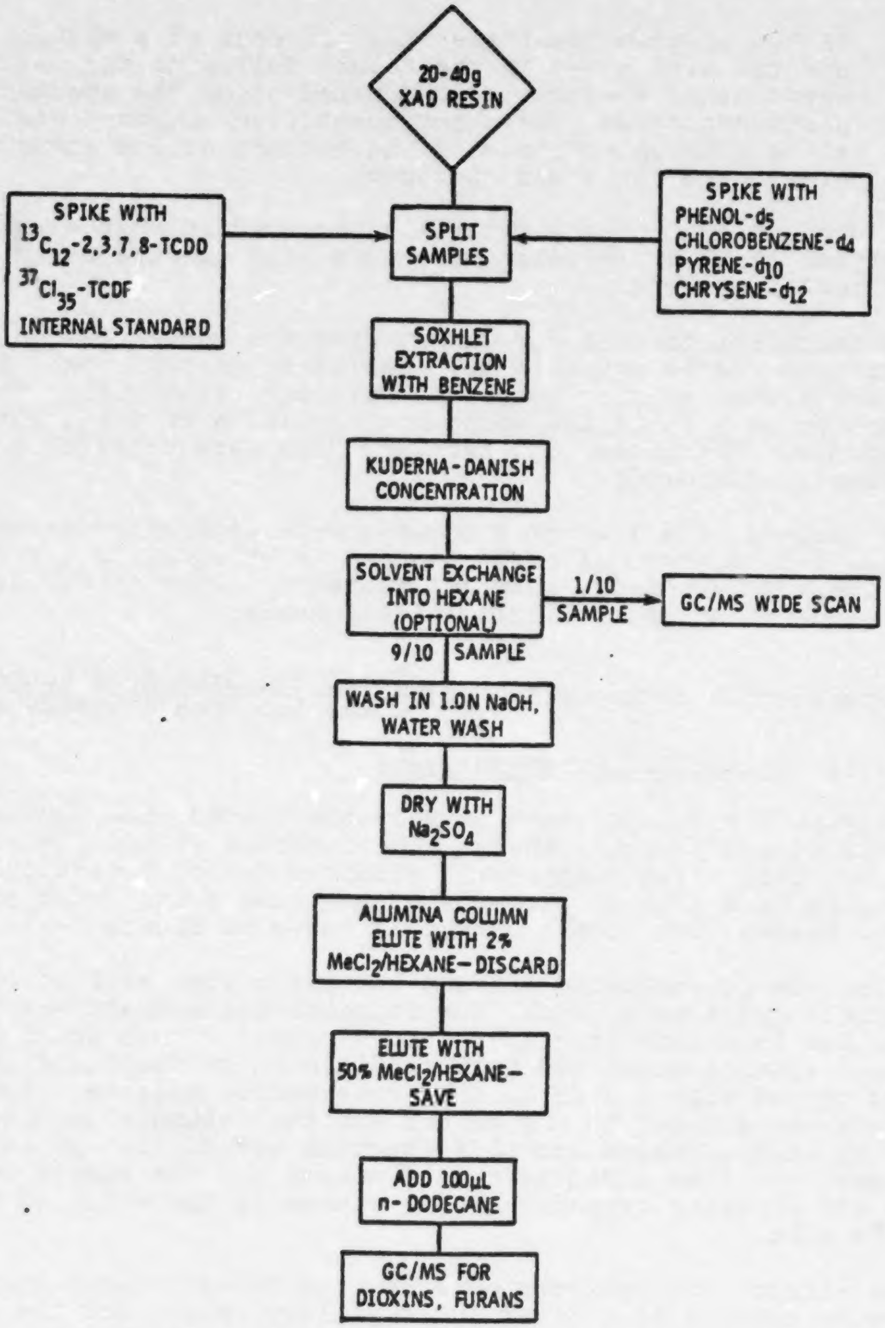

20-40g XAD RESIN
SPIKE WITH $^{13}C_{12}$-2,3,7,8-TCDD $^{37}Cl_{35}$-TCDF INTERNAL STANDARD
SPLIT SAMPLES
SPIKE WITH PHENOL-d_5 CHLOROBENZENE-d_4 PYRENE-d_{10} CHRYSENE-d_{12}
SOXHLET EXTRACTION WITH BENZENE
KUDERNA-DANISH CONCENTRATION
SOLVENT EXCHANGE INTO HEXANE (OPTIONAL)
1/10 SAMPLE
GC/MS WIDE SCAN
9/10 SAMPLE
WASH IN 1.0N NaOH, WATER WASH
DRY WITH Na_2SO_4
ALUMINA COLUMN ELUTE WITH 2% $MeCl_2$/HEXANE—DISCARD
ELUTE WITH 50% $MeCl_2$/HEXANE—SAVE
ADD 100µL n-DODECANE
GC/MS FOR DIOXINS, FURANS

Figure 3-17. Dioxin and furan analytical flow diagram of SASS-train absorbent resin.

3.4.12 Trace Element Analysis

Trace element analyses were conducted on selected Method 5 particulate samples, all waste fuels, fuel oils, baghouse dust samples, and RCRA EP toxicity extracts of baghouse dusts. Analysis was performed by using inductively coupled argon plasma emission spectroscopy (ICAP). The ICAP method is an analytical system for simultaneous multielement determinations of trace metals at the sub-ppm level in solutions. The basis of the method is atomic emission promoted by coupling the sample, nebulized to form an aerosol, with high temperature argon plasma produced by passage of argon through a powerful radio frequency field [21]. Figure 3-18 illustrates the analytical workup used for ICAP analyses.

3.4.13 Baghouse Dust

Baghouse dust samples were submitted to the EPA Extraction Procedure (EP) Toxicity test and the resulting EP extract was split and analyzed for trace elements via ICAP, and PCDD's and PCDF's to determine the suitability of land disposal of the baghouse dust collected during waste burning in a cement kiln. The EP flowchart is shown in Figure 3-19. Chloride content of the dust was determined by using ASTM D808 with selective ion electrode measurement.

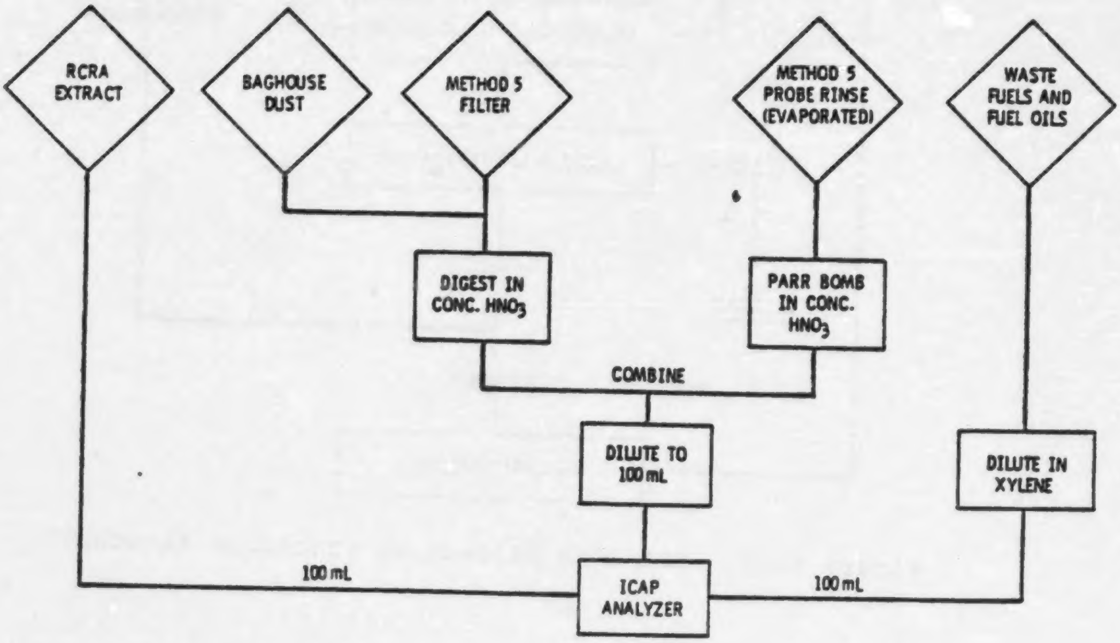

RCRA EXTRACT
BAGHOUSE DUST
METHOD 5 FILTER
METHOD 5 PROBE RINSE (EVAPORATED)
WASTE FUELS AND FUEL OILS
DIGEST IN CONC. HNO_3
PARR BOMB IN CONC. HNO_3
COMBINE
DILUTE TO 100 mL
DILUTE IN XYLENE
100 mL
ICAP ANALYZER
100 mL

Figure 3-18. ICAP analytical flow diagram.

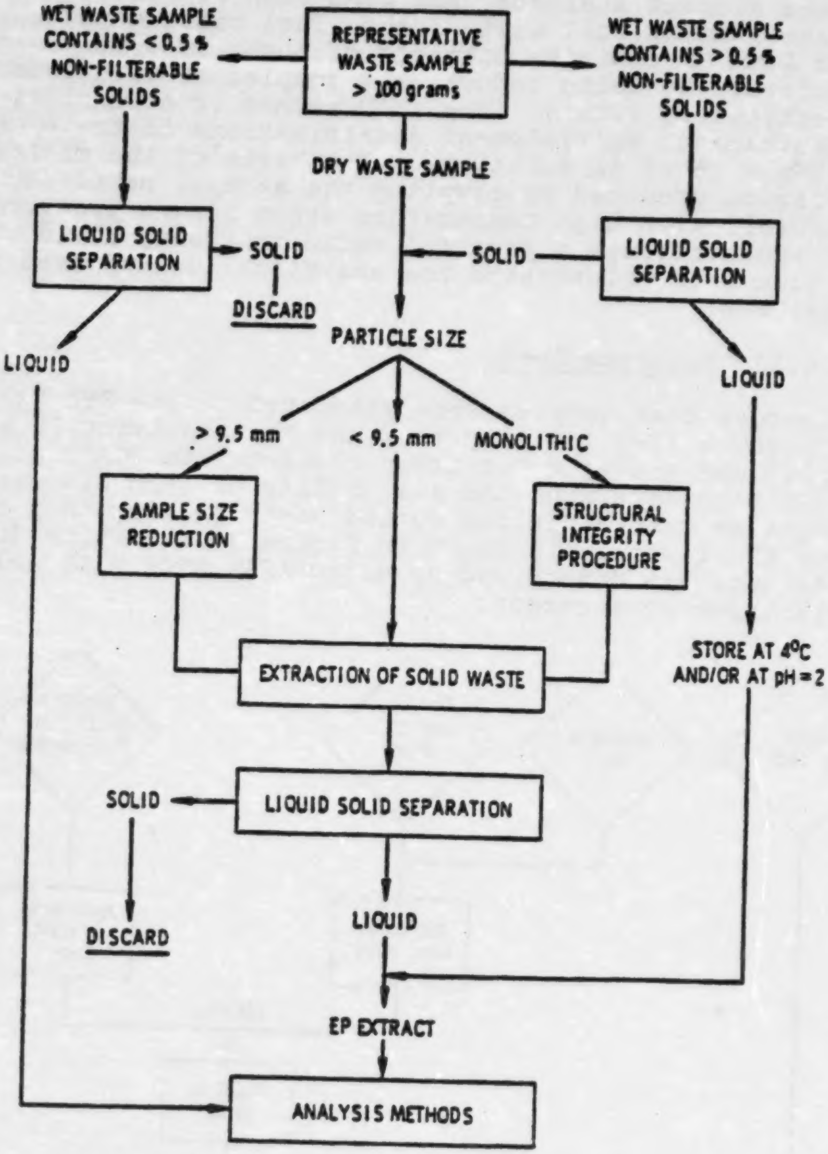

WET WASTE SAMPLE CONTAINS < 0.5 % NON-FILTERABLE SOLIDS
REPRESENTATIVE WASTE SAMPLE > 100 grams
WET WASTE SAMPLE CONTAINS > 0.5 % NON-FILTERABLE SOLIDS
DRY WASTE SAMPLE
LIQUID SOLID SEPARATION
SOLID
DISCARD
SOLID
LIQUID SOLID SEPARATION
LIQUID
PARTICLE SIZE
LIQUID
> 9.5 mm
< 9.5 mm
MONOLITHIC
SAMPLE SIZE REDUCTION
STRUCTURAL INTEGRITY PROCEDURE
EXTRACTION OF SOLID WASTE
STORE AT 4°C AND/OR AT pH = 2
SOLID
LIQUID SOLID SEPARATION
DISCARD
LIQUID
EP EXTRACT
ANALYSIS METHODS

Figure 3-19. EPA RCRA Extraction Procedure flowchart.

3.4.14 Process Water

Process water samples were taken during each test run from the water line near the slurry tanks. These samples represent "incoming" water to the plant, not plant discharges. The water is evaporated in the drying section of the cement kiln. A grab sample bottle was filled from the integrated water sampling vessel after mixing. The analysis conducted was GC/MS screening for volatile organic priority pollutants, in particular the three chlorinated POHC compounds known to be present in the waste fuel.

3.4.15 Cement Clinker

Chloride content of selected clinker product samples was measured using a high pressure O_2 bomb followed by selective ion electrode measurement.

3.4.16 Ambient Air in Surrounding Neighborhoods

Particulate concentrations of the ambient air were measured using the high volume air samplers, one located upwind and one downwind of the emission source. The samplers were run 24 hours continuously on each sampling day, and the filters were handled and weighed as stated in the Federal Register [22].

3.5 USE OF THE VALLEY MODEL FOR AMBIENT AIR SAMPLER LOCATIONS

As part of the demonstration of the use of waste fuels in a cement kiln, particulate concentrations were measured at two locations near San Juan Cement Company to assess the impact of the use of waste fuels on ambient air quality. Both the emission testing (stack) and ambient sampling were closely coordinated with the cement kiln schedule in order to determine the amount or effects of the waste fuel constituents in the kiln exhaust and the air quality. Just as particulate emission rates from Kiln No. 2 can be associated with ambient particulate concentrations, the correlation of chlorinated hydrocarbon emission rates with ambient hydrocarbon concentrations can be estimated.

Dispersion modeling of the particulate emissions plume from Kiln No. 2 at the San Juan Cement Company was performed first in order to investigate the quantity and location of the maximum ground level concentration. The results of the modeling were used to aid in placement of a downwind high-volume particulate emissions sampler during the waste fuel demonstration burn in Kiln No. 2.

The EPA VALLEY model [23] was used to predict the incremental increase in ambient particulate levels that would result from the operation of the kiln. San Juan Cement is located on a small hill. The VALLEY model has the capability for modeling rough terrain areas, stable and unstable weather conditions, and multiple or single emissions sources. It can be used to predict annual, monthly, or 24-hour averaged pollutant levels. Five types of input data are required for the VALLEY model: emission rates, meteorological data, stack parameters, receptor (topological) data, and a pollutant atmospheric reaction constant. The particulate emission rate used was 16 lb/hr.

3.5.1 Description of VALLEY Model and Input Variables

The dispersion equations used in the VALLEY model have been developed from the familiar bivariate Gaussian formulation which describes the dispersion of a pollutant from a point source. One of the two dispersion equations used in the VALLEY model is:

$$\chi(x,y,o;h,L) = 2.03 \cdot 10^{6}\ Q\ K\ ([c-y]/c)\ ([401-D]/400)C$$

$$\cdot \sum_{N=-J}^{+J} \exp\{-0.5\ [(H+2\ N\ L)/\sigma_z]^2\}$$

$$\cdot \{\exp[-(0.693\ x_p)/(3600\ u\ I)]\}/(\sigma_z\ u\ x) \qquad (15)$$

where χ = concentration in micrograms per cubic meter ($\mu g/m^3$) or parts per million (ppm), always calculated at ground level

x = the source-receptor distance (m), as projected on the mean wind vector through the source

y = the crosswind distance (m) of the receptor from a line parallel to the mean wind drawn through the source; $y \leq c$

H = plume centerline height (m) above the receptor; the receptor is always at ground level. Plume height h_o above the stack base is calculated internally, and then may be adjusted for terrain elevation at the receptor to provide H. For nonstable conditions, or over flat terrain, $H = h_o$

L = mixing height (m) above ground; L remains constant, regardless of topography

Q = the pollutant emission rate (g/s) of a given source, averaged over the period of concern

c = the crosswind arc length of the 22.5° wind sector implicit in this formulation

D = receptor elevation minus plume height, each in meters above mean sea level. The D term simulates the stable-case deflection by terrain of the plume from the sector being evaluated

$1 \text{ m} < D \leq 401 \text{ m}$ {stable conditions}

$D = 1 \text{ m}$ {neutral and unstable conditions}

C determines the units of χ:

$C = 1$ {for χ in $\mu g/m^3$; required for nongaseous pollutants}

$C = 0.0831\ T/(M\ P)$ {for gases only, to obtain χ in ppm}

where T = ambient air temperature (°K)

M = molecular weight of the gas (grams per mole)

P = ambient air pressure (millibars)

K converts concentrations from on-site to standard conditions of temperature and pressure. $K = 1013.2\ T/(298\ P)$.

N = the number of perfect reflections a parcel of air has undergone before reaching the distance of the receptor. The limits on N determine the accuracy of the term

σ_z = the standard deviation (m) of the vertical Gaussian distribution of the pollutant and $\sigma_z = f(x)$

x_p = the distance (m) from the receptor to the point source or to the center of the area source projected to the mean wind direction as was defined for x; for point sources, $x_p = x$

u = the mean wind speed (m/s) affecting the plume

I = the half-life (hr), of the pollutant and the exponential containing I is the half-life factor

In the VALLEY model, $J \leq 5$. However, as σ_z becomes large relative to L, this low limit on J can result in serious underestimates of χ. The error can be reduced to insignificance by equating J to a large value, but with a corresponding increase in computation time. Fortunately, a simple approximation to Equation (15) exists for these conditions; for distances beyond which $\sigma_z = 2\ L$ the VALLEY model uses a second equation in the form:

$$\chi(x,y,o;h,L) = 2.55 \cdot 10^6\ Q\ K\ ([c-y]/c)\ ([401-D]/400)\ C \cdot \{\exp[-(0.693\ x_p)/(3600\ u\ I)]\}/(L\ u\ x) \quad (16)$$

This simple equation provides a very good approximation to Equation (15) when J is very large and the vertical distribution of pollutants has become virtually homogeneous.

Meteorological data include stability-wind rose data (STAR data), the annual average mixing height, and ambient temperature. The STAR data are the frequencies of occurrence of six wind speed classes by sixteen wind directions by six stability categories (A to F) and define the transport and the degree of dispersion of the pollutant. The STAR data used was that from the San Juan airport, about 32 km east and the closest of four meteorological stations on Puerto Rico. The meteorological data is comprised of monthly and annual averages only, with observations taken every 8 hr. The only data available were 8 years of data from 1965-1973. The cement plant is about 8 km from the ocean, but ocean effects (not programmed into the model) are only considered for a source within 4.8 km of an ocean. The VALLEY model's effective range is about 4.8-8 km. Mixing height was ignored in the model for two reasons: mixing height has never been measured at San Juan, and the always prevalent trade winds of the tropical climate suppress any boundary layer formation.

Stack parameters (stack height and diameter, gas flow rate, exit velocity, and temperature) were available from A.T. Kearney's environmental assessment and plant permit application [3]. These were as follows:

Stack height - 57.83 ft
Stack diameter - 108 in.
Gas flow rate - 225,000 scfm
Stack gas velocity - 60 ft/s
Stack gas temperature - 450°F

For receptor data, a network of 112 receptors is established by the model. These were controlled by two factors relative to the network: (1) the geographic spacing of the receptors, through a scaling factor; and (2) the vertical spacing of the receptors through assignment of the terrain elevation at each receptor.

The particulate reaction constant was assumed to equal one, an assumption which neglects deposition and tends to increase the ground level concentrations.

Certain limitations must be considered when using the application of the VALLEY model. These limitations are as follows:

(1) Accuracy is considered to be within a factor of 2 (plus 100 percent or minus 50 percent).

(2) The range over which the model can give accurate concentration estimates is no more than a few kilometers.

This distance is dependent on the climatological and topographic conditions in the area. Plume behavior during horizontal transport is not well known beyond that variable distance. In this study, we have extended travel distance to about 5 kilometers in order to model the decreasing particulate concentration as distance increases. This distance appears reasonable for normal use of the VALLEY model but may be on the outer limits of accuracy because of the surrounding terrain. An exponential increase of standard deviation of the vertical dispersion during strong unstable stability categories, may cause an underestimation of pollutant concentration beyond this limit and may affect the modeling results even within these limits at certain receptors.

(3) The model is not designed to estimate concentrations during unusual meteorological conditions such as aerodynamic downwash and fumigation which may occur during upslope and downslope wind conditions.

(4) A straight-line transport of pollutants is assumed by the model. Hence, curvature of the plume due to pressure gradients, induced by topographic features is not simulated by the model. Since the cement plant area is a small hill (150 km) complex terrain where curvature of the plume is expected to be unusual, an underestimation of pollutant concentration using the VALLEY model would not occur compared to areas where large variations in elevation occur in short distances.

(5) The use of airport meteorological data to describe the transport and dispersion of pollutants from elevated sources during stable conditions in complex terrain is likely to involve a source of error in the application of VALLEY model.

(6) Estimated average emission rate data were used as the VALLEY input in this study. However, significant diurnal and seasonal variations in emission rates occur and can influence the levels of ambient pollutant concentrations.

(8) The VALLEY model limits the modeling to 112 receptors. These receptors are located by the program and cannot be placed at specific points of interest. As a result, the maximum concentration attainable may not fall at any of the 112 receptors modeled. Shifting the scaling factor will alter the receptor placement by the model, however, and does allow some "searching" for points of interest.

(8) If the plume height only slightly exceeds the surrounding terrain and/or the source itself lies in the lee of a hill, the pollutants may be drawn downward by down drafts in the lee of the crest and create a pollution problem at ground level. The VALLEY model does not simulate these situations.

(9) The discontinuities caused by the description of meteorological conditions by step functions, i.e., discrete classes, are smoothed in the VALLEY model across wind direction classes only. This "smoothing" causes some potential problems that may erroneously influence the model results both positively or negatively.

3.5.2 Results of the Modeling

The VALLEY model was applied to particulate emissions from Kiln No. 2 to locate the point of maximum ground level concentration. Two map scaling factors were used in relating the ambient ground level concentrations to the terrain--1:10,000 and 1:20,000. Modeling was conducted on the basis of monthly averages (for September, October, and November), annual average, and a 24-hour short-term worst-case situation. Results for each scaling factor are presented in Tables 3-5 and 3-6.

The Ambient particulate concentrations attributable to emissions from Kiln No. 2 are very minimal, with maximums ranging from 0.008 to 23 μg/m^3. The National Ambient Air Quality Standards for particulate matter are 75 μg/m^3, annual averaging time (geometric mean), and 260 μg/m^3 for a 24-hr averaging time. This result is not surprising, since a model input emission rate of 16 lb/hr corresponds to only 2.02 gm/s. Also, the stack gas temperature of 230°C (450°F) and exit velocity of 18.3 m/s (41 mph) contribute to a high plume rise and enhance dispersion.

TABLE 3-5. RESULTS OF EPA VALLEY MODEL'S PREDICTIONS OF MAXIMUM GROUND LEVEL PARTICULATE CONCENTRATIONS (SCALE 1:20,000) ATTRIBUTABLE TO KILN NO. 2

Time frame	Particulate concentration, μg/m^3	Distance from source, km	Sector
September	0.52	0.51	WSW
October	0.24	0.51	W
November	0.27	0.51	WSW
Annual	0.5	0.51	W

TABLE 3-6. RESULTS OF EPA VALLEY MODEL'S PREDICTIONS OF MAXIMUM GROUND LEVEL PARTICULATE CONCENTRATIONS (SCALE 1:10,000) ATTRIBUTABLE TO KILN NO. 2

Time frame	Particulate concentration, µg/m³	Distance from source, km	Sector
September	2.39	0.254	WSW
October	1.55	0.254	W
November	1.69	0.254	WSW
Annual	23.0	0.584	S

There are several particulate emission sources other than Kiln No. 2 at San Juan Cement which can impact surrounding ambient concentration levels. These other particulate emission sources are:

(1) Kilns No. 1 and No. 3 -- continuous emitters when operating; Kiln No. 1 has a plume opacity which is usually 15-25%.

(2) Clinker loadout -- a major dust source when the elevators and silo storage are bypassed; ground level emission source; located adjacent to the waste fuel storage tanks.

(3) Baghouse dust loading to truck -- a major dust source but intermittent; driver/operator often overfills truck, spilling baghouse dust; ground level source.

(4) Truck unloading baghouse dust -- intermittent; just dumped quickly onto waste dust pile; height of emission is >30 m above plant.

(5) Plant traffic -- continuous, minor source; a water truck wets down roadways most of the time and sprinklers are installed roadside at plant entrance road.

(6) Finish mill -- baghouse controlled with 10 m exhaust stack; intermittent exhaust with moist plume.

(7) Quarrying -- very minor emission source; stone and overburden are moist.

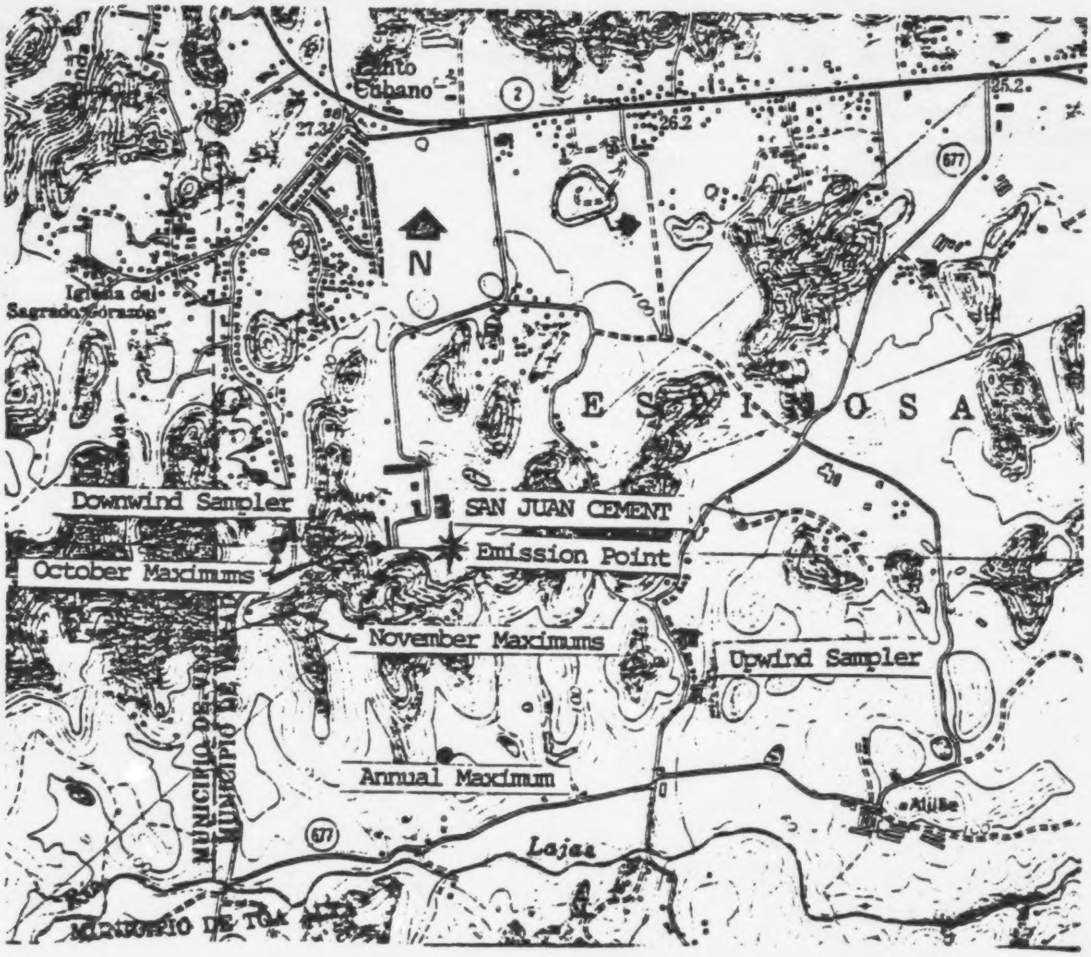
(8) Primary crushers -- very minor; feed is moist.

3.5.3 Sampling Site Locations

The locations of the two sampling stations are shown in Figure 3-20. One station (No. I) was positioned to the east of the San Juan Cement complex while the other (No. II) was to the west, or downwind of the prevailing air flow. The physical description of the sampling sites is as follows:

Station	Description
I (upwind)	Francisco Mojica residence rooftop; 30 m west from Road No. 677; 5.5 m from ground; Sector Chicharos, Bo. Rio Lajas, Dorado, 0.75 km east of the stack of Kiln No. 2.
II (downwind)	Emilio Marzán residence rooftop; 17 m east from Road No. 679; 13 ft from ground, Bo. Espinosa, Dorado, 0.5 km west of the stack of Kiln No. 2.

The general location of Station No. II was determined by MRC with the use of the air quality dispersion model (VALLEY). The residence of Emilio Marzán is located almost exactly at the point of maximum concentration as detected by the model. As discussed earlier, the downwind station was oriented to determine the influence, if any, of the emissions from San Juan Cement Kiln No. 2 where the project was being conducted.



Santo Cubano
2
27.3
26.2
25.2
677
N
Iglesia del Sagrado Corazón
E S P I N O S A
Downwind Sampler
SAN JUAN CEMENT
Emission Point
October Maximums
November Maximums
Upwind Sampler
Annual Maximum
MUNICIPIO DE
MUNICIPIO DE
677
Lajas
Aljibe
MUNICIPIO DE TOA ALTA

Figure 3-20. Location of sampling sites and computer-selected points.

Scale: 1 inch = 0.5 kilometers

■ Upwind site ● Computer selections
▲ Downwind site

Source: U.S. Geological Survey Map, Vega Alta, P.R., 1969

SECTION 4

EMISSION TESTING RESULTS

The design of the demonstration burn incorporated a matrix wherein the amount of chlorine in the waste and waste feed rate to the kiln were varied. A comprehensive sampling and analytical program was also conducted in order to meet the project objectives which included determining the destruction and removal efficiencies of the principal organic hazardous constituents (POHC's) in the waste fuel, the products of incomplete combustion (PIC's), the difference in emission levels of conventional pollutants, the effects on clinker quality and kiln refractory lining integrity, the effects on ambient air quality, the presence or absence of dioxins and dibenzofurans, the effects of transition from normal kiln operation to waste burning, the chlorine material balance, possible monitoring techniques for enforcement purposes, and the magnitude of possible fuel savings.

4.1 DATA COLLECTION PROCEDURES

Data were collected during each burn to document the waste fuel and fuel oil flowrates and kiln operation as it affected the waste burning. (Note--prior to Monsanto Research Corporation's assuming responsibility for the waste fuel firing, no data were recorded or available on the waste firing rates and kiln operation for waste batches #1 and #2).

The waste and fuel rate data collected at 15 minute intervals were clock time, elapsed run time, flow totalizer meter readings, the two waste fuel flowmeter instantaneous readings, waste fuel temperature, line pressure before and after the main control valve, fuel oil flow rate, and waste storage tank levels. The kiln production data recorded were burning zone temperature, maximum and minimum kiln shell temperature, exit gas temperature, baghouse inlet gas temperature, kiln exhaust oxygen percentage, primary, secondary, and hood air measurements, slurry feed rate, and clinker production rate. Additionally, continuous recording charts were obtained from the control room instrumentation for burning zone temperature, kiln shell temperature, exit gas temperature, and fuel oil flow rate.

The waste fuel flow rate was measured by three different methods: flow totalizer, magnetic flowmeter, and orifice meter. The flow totalizer was used to give a close estimation (uncalibrated) of the amount of waste fuel consumed as well as a quick calculation of the average rate. The magnetic flowmeter was used to give a calibrated flow rate and allow the precise setting and adjustment of the main control valve. Redundant measurement of calibrated flow rate was accomplished with an orifice meter coupled to a circular recorder chart placed in the control room to enable the kiln operators to determine waste fuel flow rate.

4.2 WASTE FUEL ANALYSES

A detailed summary of the waste fuel compositions of each of the six waste batch shipments is given in Table 4-1. A seventh waste batch was burned and tested, which was a mixture of Batches 4 and 6. The techniques of analysis were described in Section 3.1.

ASTM analytical methods were also used on selected waste fuel samples to determine the sulfur, nitrogen, and chlorine contents for comparison with the $(GC)^2/MS$ wide scan analyses. Table 4-2 presents these results which illustrate very low levels of sulfur and nitrogen. Chlorine levels determined by ASTM D808 were 20-40% off the values calculated from the GC/MS wide scan analysis.

Elemental analysis of the waste fuel batches, given in Table 4-3, showed no surprises. Waste Batch 3 had higher levels of tin, lead, and vanadium than the other batches.

4.3 DEMONSTRATION BURN TEST RUNS

The results of the waste fuel burn tests conducted are summarized in Table 4-4. Waste flow rate into the kiln had to be limited in the case of waste batch #4 because the high chlorine content affected cement product quality and kiln lining integrity.

4.4 EMISSION TEST RESULTS

A total of five baseline tests (no waste fuel burned) were completed in order to determine the differences in stack emissions between waste firing and normal operation. Four of the baseline testing days involved EPA Method 5 testing and the fifth test was a SASS run.

When waste fuel was burned, eleven tests on seven different waste fuel batches were completed. These included SASS runs on waste batch numbers 3, 4, and 6; and EPA Method 5 runs on seven waste fuel burn tests.

Tables 4-5 and 4-6 summarize the results of stack emission testing at San Juan Cement. The numbering system is as follows: BW designates a baseline test; a subsequent number indicates the test run number; W number indicates the waste fuel batch number; and the

TABLE 4-1. SUMMARY OF WASTE FUEL ANALYSES FOR CEMENTO SAN JUAN DEMONSTRATION BURN (volume basis)

Compound	Batch 1, vol %	Batch 2, vol %	Batch 3, vol %	Batch 4, vol %	Batch 5, vol %	Batch 6, vol %	Batch 4/6, vol %	Density, g/mL	TLV,[c] mg/m^3
Water	<1.0	4.1	4.3	8.9	23.0	2.0	NA	1.000	-[d]
Methanol	10.4	7.1	13.9	6.2	10.9	ND[a]	NA	0.7914	260
Ethanol	0.8	3.2	8.6	4.7	16.8	5.6	NA	0.7983	1,900
Acetone	14.2	12.2	11.2	10.5	4.6	2.2	NA	0.7899	2,400
2-Propanol	4.7	5.2	5.3	4.5	3.1	1.6	NA	0.7855	500
Methylene chloride	24.4	16.9	12.0	12.1	1.4	5.0	5.1	1.3266	360
Hexane isomers	3.9	3.2	1.8	1.5	ND	1.5	NA	0.6532	-[d]
3-Methylpentane	5.4	4.6	2.7	3.2	ND	3.6	NA	0.6645	-[d]
Hexane	19.8	17.3	7.2	8.5	5.9	15.7	NA	0.6603	1,800
Chloroform	1.0	0.8	3.4	5.4	4.0	0.1	0.9	1.4832	50[f]
Ethyl acetate	4.0	14.0	9.0	6.6	3.5	22.7	NA	0.9003	1,400
Methyl acetate	ND	NA[b]	0.4	<1.0	ND	ND	NA	0.9330	610
Carbon tetrachloride	0.8	0.6	1.4	10.2	7.8	0.01	1.5	1.5940	35[f]
Benzene	0.4	0.4	0.2	0.3	0.1	0.05	NA	0.8787	35[f]
Hexamethyl disiloxane	0.1	ND	ND	NA	NA	NA	NA	0.8923	-[d]
Toluene	0.2	0.1	0.02	<0.5	ND	ND	NA	0.8669	375
Acrylonitrile	ND	1.0	1.1	<0.7	1.0	ND	NA	0.8060	5[f]
Methyl ethyl ketone	NA	NA	0.08	1.1	NA	NA	NA	0.8054	590
C_5-benzene isomer	NA	NA	1.33	0.5	0.9	2.2	NA	0.90[e]	-[d]
C_6-benzene isomer	NA	NA	ND	NA	ND	23.8	NA	0.90[e]	-[d]
Sec-butyl ethylbenzene	NA	NA	1.23	1.7	NA	NA	NA	0.90[e]	-[d]

(continued)

TABLE 4-1 (continued)

Compound	Batch 1, vol %	Batch 2, vol %	Batch 3, vol %	Batch 4, vol %	Batch 5, vol %	Batch 6, vol %	Batch 4/6, vol %	Density, g/mL	TLV,[c] mg/m³
Xylene isomers	NA	NA	0.24	NA	NA	ND	NA	0.87[e]	435
Dimethylphenol isomer	NA	NA	0.04	NA	ND	ND	NA	0.90[e]	-[d]
1,1'-(1,2-ethanediol)bis-4-methoxybenzene	NA	NA	0.23	NA	NA	NA	NA	0.90[e]	-[d]
Unknowns	8.9	9.3	14.3	11.9	17.9	13.9	NA		
PCBs, ppm	<50	<100	<100	<100	<100	<100	<100		
Pesticides[g], ppm	<100	<100	<100	<100	<100	<100	<100		
Properties									
Btu content, Btu/lb	11,188	11,198	11,022	10,099	4,546	13,098	NA		
Specific gravity	NA	NA	0.9948	0.9885	1.0092	0.9163	0.9410		
Chlorine content, wt %	32.0	22.9	21.4	35.1	18.7	6.5	10.1		
Ash content, wt %	0.30	0.20	0.38	0.23	0.31	0.046	NA		

[a] ND = not detected, generally <0.1% by volume.

[b] NA = not analyzed.

[c] Threshold limit value for workplace air.

[d] No TLV assigned to this compound or isomer.

[e] Estimated values.

[f] Suspected or known carcinogen.

[g] As per priority pollutant list.

TABLE 4-2. WASTE FUEL CONTENTS OF NITROGEN, SULFUR, AND CHLORINE

Element	Waste batch 1	Waste batch 4	Waste batch 6	Method
Percent S	0.08	1.89	0.22	ASTM D129
Percent N	1.25	NA	2.33	Kjeldahl
Percent Cl	18.9[a]	NA	7.9	ASTM D808 (followed by selective ion electrode measurement)

[a] Sample was not homogeneous.

TABLE 4-3. ELEMENTAL ANALYSES OF WASTE FUELS USED AT SAN JUAN CEMENT COMPANY DEMONSTRATION BURN (μg/mL)

Element	Waste fuel							
	W1-1	W2-1	W3	W4-2	W4-4	W5	W6	W6-1
Ag	<0.798	<0.799	2.53	<0.793	<0.797	<0.791	1.13	1.15
Ca	<0.100	5.45	<0.99	<0.099	0.114	<0.099	0.555	0.200
Fe	4.05	12.6	<0.682	104.0	272.0	3.32	2.49	2.99
Na	21.2	20.0	49.9	19.7	17.9	25.4	27.1	<14.9
Si	123.0	311.0	5.76	298.0	478.0	24.0	20.6	124.0
Zn	2.71	4.09	<0.682	4.47	5.8	2.85	3.13	3.05
Al	1.52	1.68	2.24	1.84	1.96	1.46	3.26	2.05
Cd	0.737	0.753	<0.390	0.955	1.09	0.785	1.36	0.691
Mg	1.63	1.62	<0.974	1.62	1.61	1.60	1.67	1.64
Ni	5.93	6.29	31.2	6.45	7.71	5.58	5.76	7.84
Sn	3.15	1.399	146.1	3.21	4.53	2.36	1.86	4.92
B	12.2	12.8	43.1	15.7	29.6	12.1	13.0	13.5
Cr	1.57	1.73	<0.974	5.06	5.52	1.73	2.01	1.66
Mn	0.247	0.276	0.487	0.306	0.350	0.266	0.296	0.241
P	18.1	32.8	35.1	69.1	77.9	16.5	12.0	21.2
Ti	0.549	0.536	0.682	0.570	0.474	0.638	0.762	0.413
Ba	1.15	1.14	<0.682	1.16	1.25	1.22	1.27	0.984
Cu	1.40	2.30	1.56	4.93	11.8	1.45	2.07	2.16
Mo	5.51	5.52	2.24	5.97	6.39	5.43	5.81	6.02
Pb	1.13	1.33	25.7	1.93	2.64	<1.09	2.11	2.14
V	1.20	1.26	7.39	1.65	1.42	1.17	1.43	1.23

TABLE 4-4. SUMMARY OF WASTE FUEL BURN TESTS AT SAN JUAN CEMENT COMPANY

			POHC's in waste fuel					
Date	Waste and run no.	Calibrated flow rate, m^3/s (gpm)	Methylene chloride, wt %	Chloroform, wt %	Carbon tetrachloride, wt %	Total chlorine, wt %	Average burn zone temperature, °C (°F)	Major sampling effort of run
10/29/81	W1-1	$1.89^{a} \times 10^{-4}$(3.00)	35.1	1.6	1.4	32.0	1,038(1,900)	EPA Method 5
11/10/81	W2-1	$3.16^{a} \times 10^{-4}$(5.00)	24.8	1.3	1.1	22.9	1,368(2,495)	EPA Method 5
11/16/81	W1-2	3.28×10^{-4}(5.20)	35.1	1.6	1.4	32.0	982(1,800)	EPA Method 5
12/3/81	W3-1	1.28×10^{-4}(2.02)	17.2	5.4	2.4	21.4	1,268(2,315)	SASS
12/4/81	W3-2	2.30×10^{-4}(3.65)	17.2	5.4	2.4	21.4	1,354(2,469)	EPA Method 5
12/4/81	W3-3	2.75×10^{-4}(4.35)	17.2	5.4	2.4	21.4	1,376(2,509)	EPA Method 5
12/8/81	W4-1	1.10×10^{-4}(1.75)	15.8	7.9	16.1	35.1	1,121(2,050)	HCl and GC/EC
12/9/81	W4-2	1.10×10^{-4}(1.74)	15.8	7.9	16.1	35.1	1,102(2,016)	EPA Method 5
12/10/81	W4-3	2.18×10^{-4}(3.45)	15.8	7.9	16.1	35.1	1,398(2,548)	EPA Method 5
1/13/82	W4-4	1.07×10^{-4}(1.70)	15.8	7.9	16.1	35.1	1,405(2,561)	SASS
1/26/82	W4-5	2.01×10^{-4}(3.18)	15.8	7.9	16.1	35.1	1,343(2,450)	GC/EC
1/28/82	W6-1	9.91×10^{-5}(1.57)	7.6	0.17	0.02	6.5	1,386(2,526)	SASS
2/7/82	W5-1	9.15×10^{-5}(1.45)	1.9	6.1	12.7	18.7	1,389(2,532)	GC/EC and CO
2/8/82	W5-2	1.14×10^{-4}(1.81)	1.9	6.1	12.7	18.7	1,368(2,495)	GC/EC and CO
2/9/82	W4/6-1	2.28×10^{-4}(3.62)	7.8	1.5	2.45	10.1	1,362(2,483)	GC/EC and CO
2/10/82	W4/6-2	3.50×10^{-4}(5.55)	7.8	1.5	2.45	10.1	1,266(2,310)	GC/EC and CO
2/10/82	W4/5-3	8.39×10^{-5}(1.33)	7.8	1.5	2.45	10.1	1,482(2,700)	GC/EC and CO
2/12/82	W4/6-4	1.52×10^{-4}(2.41)	7.8	1.5	2.45	10.1	1,399(2,550)	GC/EC and CO
2/12/82	W4/6-5	3.74×10^{-4}(5.92)	7.8	1.5	2.45	10.1	1,476(2,688)	GC/EC and CO

[a] Estimated values.

TABLE 4-5. SUMMARY OF STACK EMISSION TESTING RESULTS (metric units)

Parameter/pollutant	Run no./Date									
	BW-1 10/14/81	BW-2 10/15/81	BW-3 10/27/81	W1-1 10/29/81	BW 10/30/81	BW 11/2/81	BW-4 11/8/81	BW 11/9/81	W2-1 11/10/81	BW 11/11/81
Stack temperature, °C	167	170	172	186			180		168	
Stack velocity, m/min	686	685	680	587			671		584	
Volumetric flow rate, dncmpm	1,782	1,783	1,815	1,548			1,713		1,619	
Volumetric flow rate, acmpm	4,068	4,065	4,032	3,480			3,984		3,465	
Moisture, %	33.5	32.8	30.8	29.6			33.1		32.3	
Oxygen, %	11.7	12.8	12.3	13.0			11.5		12.0	
Carbon dioxide, %	17.5	13.5	13.7	12.6			16.7		16.0	
Particulate loading, g/dncm	0.0787	0.0616	0.0574	0.1025			0.1759		0.2558	
Particulate emissions, kg/hr	8.4	6.6	6.3	9.5			18.1		24.8	
SO_2, ppm	218	91	407	874			400		350	
SO_2 emissions, kg/hr	61.0	25.5	116.8	212.4			107.6		98.0	
NO_x, ppm	112	211	93				129		66	
NO_x emissions, kg/hr	22.8	42.7	19.2				25.1		14.2	
CO, ppm				378		35	41	60	260	240
CO, std. dev.				417		81	62	137	341	357
CO, range, ppm				93-2,670		0-291	0-276	4-645	6->1,000	15->1,000
THC, ppm			8.9	16.0	13.5	7.7	8.6	4.4	9.1	9.3
THC, std. dev.			10.2	6.8	2.0	6.3	2.4	2.3	1.6	2.0
THC, range, ppm			1-35	7-44	9-18	0-39	3-16	1-94	5-17	6-16
Hydrogen chloride emissions, kg/hr			<0.011				0.16			

(continued)

TABLE 4-5 (continued)

Parameter/pollutant	BW 11/12/81	W-2 11/15/81	W1-2 11/16/81	BW 11/17/81	BW-SASS 11/18/81	W3-SASS-1 12/3/81	W3-2 12/4/81	W3-3 12/4/81	W4-1 12/8/81	W4-2 12/9/81
	Run no./Date									
Stack temperature, °C			176		180	165	170	166		159
Stack velocity, m/min			723		636	610	665	650		652
Volumetric flow rate, dncmpm			1,891		1,622	1,594	1,739	1,698		1,796
Volumetric flow rate, acmpm			4,289		3,776	3,617	3,945	3,859		3,870
Moisture, %			29.7		33.3	33.9	33.1	33.7		31.1
Oxygen, %			12.0		12.3	10.4	10.6	10.6		11.3
Carbon dioxide, %			15.5		15.1	17.3	15.0	16.4		13.6
Particulate loading, g/dncm			0.0719				0.0673	0.0587		0.0745
Particulate emissions, kg/hr			8.2				7.0	6.0		8.0
SO_2, ppm			263					548		485
SO_2 emissions, kg/hr			67.0					143.4		137.1
NO_x, ppm			49			87	42	51		45
NO_x emissions, kg/hr			8.9			15.8	8.3	9.8		9.3
CO, ppm	173	24	308	349	263	289				
CO, std. dev.	317	52	379	267	259	360				
CO, range, ppm	0->1,000	0->1,000	0->1,000	162->1,000	1->1,000	1->1,000				
THC, ppm	8.2		11.8	9.6	4.6	12.3	13.2	14.7	11.9	
THC, std. dev.	1.9		4.9	2.7	1.6	2.7	3.4	2.8	4.8	
THC, range, ppm	5-14		5-43	6-19	2-10	7-22	7-21	7-21	5-24	
Hydrogen chloride emissions, kg/hr			0.30			0.30	0.74	0.56	0.54	0.25

(continued)

TABLE 4-5 (continued)

Parameter/pollutant	W4-3 12/10/81	W4-SASS-4 1/14/82	W6-SASS-1 1/26/82	W5-1 2/07/82	W5-2 2/08/82	W4/6-1 2/09/81	W4/6-2 2/10/82	W4/6-4 2/12/82	W4/6-5 2/12/82
	Run no./Date								
Stack temperature, °C	171	158	156						
Stack velocity, m/min	699	645	688						
Volumetric flow rate, dncmpm	2,087	2,023	1,933						
Volumetric flow rate, acmpm	4,146	3,824	4,083						
Moisture, %	23.3	21.9	30.6						
Oxygen, %	14.5	12.3	11.5						
Carbon dioxide, %	10.8	15.3	14.5						
Particulate loading, g/dncm	0.0631								
Particulate emissions, kg/hr	7.9								
SO_2, ppm	191								
SO_2 emissions, kg/hr	62.6								
NO_x, ppm	81	57	134						
NO_x emissions, kg/hr	19.2	13.1	29.5						
CO, ppm		492	87	123	305	738	559	468	205
CO, std. dev.		373	208	270	324	300	383	394	358
CO, range, ppm		0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000
THC, ppm									
THC, std. dev.									
THC, range, ppm									
Hydrogen chloride emissions, kg/hr	0.45	<0.012	0.063						

Note: Blanks indicate no measurement taken.

TABLE 4-6. SUMMARY OF STACK EMISSION TESTING RESULTS (English units)

Parameter/pollutant	Run no./Date BW-1 10/14/81	BW-2 10/15/81	BW-3 10/27/81	W1-1 10/29/81	BW 10/30/81	BW 11/2/81	BW-4 11/8/81	BW 11/9/81	W2-1 11/10/81	BW 11/11/81
Stack temperature, °F	333	339	342	367			356		348	
Stack velocity, ft/s	37.5	37.5	37.1	32.1			36.7		39.5	
Volumetric flow rate, dscfm	62,979	63,019	64,462	54,703			60,562		66,824	
Volumetric flow rate, acfm	143,784	143,684	142,438	122,983			140,799		151,604	
Moisture, %	33.5	32.8	30.88	29.6			33.1		32.3	
Oxygen, %	11.7	12.8	12.3	13.0			11.5		12.0	
Carbon dioxide, %	17.5	13.5	13.7	12.6			16.7		16.0	
Particulate loading, gr/dscf	0.0344	0.0269	0.0251	0.0448			0.0768		0.2382	
Particulate emissions, lb/hr	18.6	14.5	13.9	21.0			39.9		98.4	
SO_2, ppm	218	91	407	874			400		350	
SO_2 emissions, lb/hr	134.6	56.2	257.5	468.3			237.2		216.1	
NO_x, ppm	112	211	93				129		66	
NO_x emissions, lb/hr	50.2	94.2	42.3				55.4		31.4	
CO, ppm				378		35	41	60	260	240
CO, std. dev.				417		81	62	137	341	357
CO, range, ppm				93-2,670		0-291	0-276	4-465	6->1,000	15->1,000
THC, ppm			8.9	16.0	13.5	7.7	8.6	4.4	9.1	9.3
THC, std. dev.			10.2	6.8	2.0	6.3	2.4	2.3	1.6	2.0
THC, range, ppm			1-35	7-44	9-18	0-39	3-16	1-94	5-19	6-16
Hydrogen chloride emissions, lb/hr			<0.0245				0.35			

(continued)

TABLE 4-6 (continued)

	Run no./Date									
Parameter/pollutant	BW 11/12/81	W-2 11/15/81	W1-2 11/16/81	BW 11/17/81	BW-SASS 11/18/81	W3-SASS-1 12/3/81	W3-2 12/4/81	W3-3 12/4/81	W4-1 12/8/81	W4-2 12/9/81
Stack temperature, °F			334		356	330	338	332		318
Stack velocity, ft/s			31.9		34.8	33.3	36.4	35.6		35.7
Volumetric flow rate, dscfm			57,220		57,318	56,309	61,459	59,963		63,489
Volumetric flow rate, acfm			122,465		133,430	127,776	139,412	136,373		136,777
Moisture, %			29.7		33.3	33.9	33.1	33.7		31.1
Oxygen, %			12.0		12.3	10.4	10.6	10.6		11.3
Carbon dioxide, %			15.5		15.1	17.3	15.0	16.4		13.6
Particulate loading, gr/dscf			0.0767				0.0294	0.0257		0.0326
Particulate emissions, lb/hr			31.7				15.5	13.2		17.7
SO_2, ppm			263					548		485
SO_2 emissions, lb/hr			147.7					316.1		302.3
NO_x, ppm			49			87	42	51		45
NO_x emissions, lb/hr			19.7			34.8	18.4	21.6		20.4
CO, ppm	173	24	308	349	263	289				
CO, std. dev.	317	52	368	167	259	360				
CO, range, ppm	0->1,000	0->1,000	0->1,000	162->1,000	1->1,000	1->1,000				
THC, ppm	8.2		11.8	9.6	4.6	12.3	13.2	14.7	11.9	
THC, std. dev.	1.9		4.9	2.7	1.6	2.7	3.4	2.8	4.8	
THC, range, ppm	5-14		5-43	6-19	2-10	7-22	7-21	7-21	5-24	
Hydrogen chloride emissions, lb/hr			0.67			0.66	1.63	1.24	1.18	0.56

(continued)

TABLE 4-6 (continued)

Parameter/pollutant	W4-3 12/10/81	W4-SASS-4 1/14/82	W6-SASS-1 1/26/82	W5-1 2/07/82	W5-2 2/08/82	W4/6-1 2/09/81	W4/6-2 2/10/82	W4/6-4 2/12/82	W4/6-5 2/12/82
	Run no./Date								
Stack temperature, °F	339	317	314						
Stack velocity, ft/s	38.2	35.3	37.6						
Volumetric flow rate, dscfm	73,745	71,484	68,267						
Volumetric flow rate, acfm	146,538	135,164	144,166						
Moisture, %	23.3	21.9	30.6						
Oxygen, %	14.5	12.3	11.5						
Carbon dioxide, %	10.8	15.3	14.5						
Particulate loading, gr/dscf	0.0276								
Particulate emissions, lb/hr	17.4								
SO_2, ppm	191								
SO_2 emissions, lb/hr	138.1								
NO_x, ppm	81	57	134						
NO_x emissions, lb/hr	42.3	28.8	65.0						
CO, ppm		492	87	123	305	738	559	468	205
CO, std. dev.		373	208	270	324	300	383	394	358
CO, range, ppm		0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000	0->1,000
THC, ppm									
THC, std. dev.									
THC, range, ppm									
Hydrogen chloride emissions, lb/hr	0.99	<0.0272	0.14						

Note: Blanks indicate no measurement taken.

subsequent number designates the test run number on that particular waste batch. On some days no test runs with extractive sampling were made but the continuous analyzers and GC/EC were operating; these days are designated similarly but without a run number assigned.

4.4.1 Opacity

Plume opacity of kiln #2 was monitored periodically in order to ensure that the plant was remaining in compliance with regulations (less than 20% average opacity). The plume was a white, continuous dust plume. Readings were taken during test runs BW-4, W1-2, W3-3, and W4-4, and results were that kiln #2 remained in compliance.

4.4.2 Particulate Emissions

Particulate emissions remained at a low level during both baseline and waste firing periods. Only run number W2-1 exceeded the hazardous waste incinerator particulate emissions standard of 0.18 g/dncm. This test was two days after a baseline test (BW-4) in which a grain loading of 0.176 g/dncm was measured, and was due to poor baghouse performance rather than waste firing. Shortly afterward, several fabric filter bags were replaced in the control device and particulate concentrations returned to levels of 0.05 to 0.10 g/dncm.

The average particulate stack gas concentration during baseline testing was 93.4 ± 65.2 mg/m^3 (95% confidence limits); during waste firing the average particulate concentration was 99.1 ± 65.2 mg/m^3. Both runs BW-4 and W2-1 could be discarded as outliers according to the Dixon Outlier or Q-test from each data set, but were allowed to remain because the values measured were the result of decreased baghouse performance rather than attributable to waste burn or testing variables. See Section 4.4.8 for a discussion of differences between baseline and waste firing emissions.

4.4.3 Sulfur Dioxide Emissions

Negligible amounts of sulfur were found in the waste fuels; the No. 6 fuel oil used to fire the kiln contained 2.15% sulfur. The maximum amount of SO_2 emissions possible is:

$$\frac{24 \text{ gal oil}}{\text{min}} \times \frac{8.25 \text{ lb}}{\text{gal}} \times \frac{0.0215 \text{ lb S}}{\text{lb oil}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{2 \text{ lb } SO_2}{\text{lb S}} = 511 \text{ lb/hr or } 232 \text{ kg/hr}$$

Alternately, an estimation method [24] for maximum SO_2 emissions based on fuel analyses and SO_2/CO_2 relations would predict 211 kg/hr.

Emissions of SO_2 ranged from 25.5 to 212 kg/hr and averaged 103 kg/hr during the demonstration program. Calculations based on the AP-42 emission factor [25] for cement kilns with baghouse APC indicate that about 97 kg/hr SO_2 would be expected, and the test results give a favorable comparison. Some "scrubbing" of SO_2 naturally occurs in cement kilns because of the presence of an alkaline environment in both the kiln and baghouse dust which contain Na, K, and Ca for forming sulfates. The SO_2 emission factor takes into account reactions with alkaline dust in the kiln and, when baghouses are used, about 50% more SO_2 is removed because of additional reactions of acid gas with alkaline particulate filter cake.

The average SO_2 stack gas concentration during baseline testing was 279 ± 243 ppm (743 mg/m^3), and during waste firing was 450 ± 245 ppm (1198 mg/m^3).

4.4.4 Nitrogen Oxides Emissions

Emissions of NO_x averaged 18.3 kg/hr and ranged from 8 to 43 kg/hr (42 to 211 ppm) during the demonstration program. Expected emission rates from emission factor calculations would be 39 kg/hr [25], and cement kilns normally have from 100-1500 ppm NO_x stack gas concentrations. The average NO_x emission rate during baseline testing was 27.5 kg/hr (136 ± 83 ppm), and during waste firing was 14.2 kg/hr (68 ± 23 ppm).

4.4.5 Total Hydrocarbon Emissions

Emissions of total hydrocarbons were measured continuously and remained steady regardless of whether waste fuel was burned. The average THC stack gas concentration during baseline testing was 8.3 ± 2.1 ppm, and during waste firing was 12.7 ± 2.1 ppm.

4.4.6 Hydrogen Chloride Emissions

As with sulfur dioxide emissions, some scrubbing of HCl emissions occurs within the cement kiln. Levels of HCl emissions ranged from below detection limits (less than 0.1015 mg/m^3) to 7.07 mg/m^3. The average emission level during waste firing was 3.32 ± 1.74 mg/m^3.

4.4.7 Carbon Monoxide Emissions

Carbon monoxide emissions are an indicator of incomplete combustion in the cement kiln. When the kiln combustion was stable, emission levels stayed below 10 ppm. However, any process fluctuation or change in kiln variables caused a momentary excursion in CO emissions to levels greater than 1,000 ppm (0.1%), even during baseline testing. The maximum level of CO measurable (with calibration gas standards) during this demonstration program was

1,000 ppm, and, hence, the >1,000 ppm excursions were not measured and could only be reported as >1,000 ppm. For the purposes of averaging, a value of 1,000 ppm was used to compute the values shown in Table 4-5.

A commonly occurring effect of waste fuel introduction to the kiln is shown in Figure 4-1, and illustrates the approximately one-hour transition period and effect on CO emissions when waste fuel is burned. From 0800 hours to 0905 hours, the kiln was not burning waste fuel and CO emission levels hover at 0-40 ppm, indicative of stable kiln operation. As the waste fuel is introduced the CO levels rise rapidly beyond 1,000 ppm for approximately 20 min and return to levels below 100 ppm as the kiln operators stabilize operation.

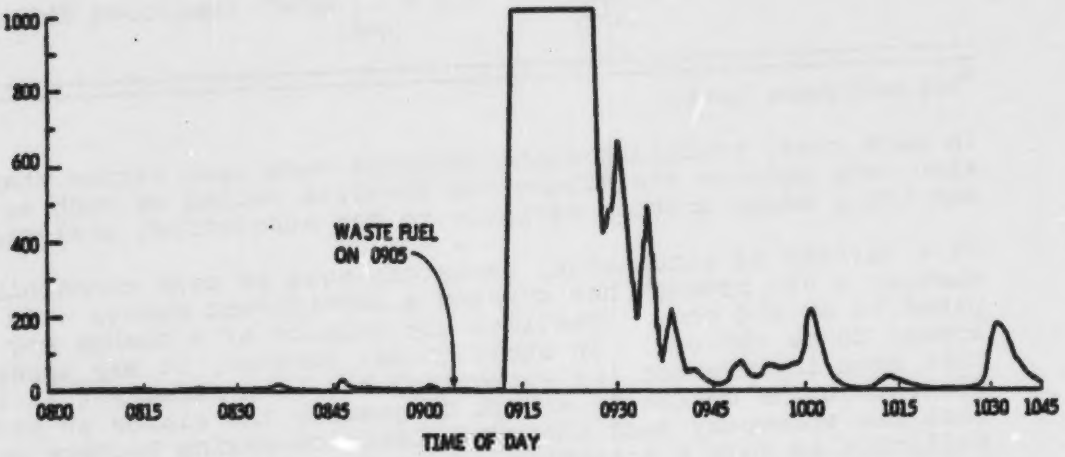


Figure 4-1. Illustration of waste fuel burn transition period effect on carbon monoxide emissions, Run W6-SASS-1, 28 January 1982, San Juan Cement Company.

4.4.8 Statistical Testing for Significant Change

Measurements of several conventional pollutants were made repeatedly during the program to determine the difference in emissions between baseline operation (no hazardous waste fed to the kiln) and waste fuel burns. Table 4-7 presents the comparisons for particulate, NO_x, SO_2, total hydrocarbons, and HCl emissions.

TABLE 4-7. COMPARISON OF POLLUTANT LEVELS BETWEEN NORMAL OPERATION AND WASTE FUEL FIRING IN CEMENT KILN NO. 2, SAN JUAN CEMENT COMPANY

Pollutant	Mean loading: Baseline	Mean loading: Waste firing	Statistical significance at 95% degree of certainty
Particulate matter	93 ± 65 mg/m^3[a] (n=4)	99 ± 65 mg/m^3 (n=7)	No significant difference
NO_x	136 ± 83 ppm (n=4)	68 ± 23 ppm (n=9)	Significant difference
SO_2	279 ± 243 ppm (n=4)	450 ± 245 ppm (n=6)	Significant difference
Total hydrocarbons	8.3 ± 2.1 ppm (n=9)	12.7 ± 2.1 ppm (n=7)	Significant difference
HCl	0.82 mg/m^3 (n=2)	3.3 ± 1.7 mg/m^3 (n=9)	Significant difference

[a] 95% confidence level.

In each case, pollutant concentrations were used rather than emission rate because the volumetric flowrate varied as much as 30%, and hence added another variable to the statistical analysis.

In a variety of situations, decisions must be made concerning whether a new process has created a significant change when compared to an old one. Sometimes the results of a change may appear to be obvious. In other cases, however, it may appear that some improvement (or worsening) has been made, but it is not clear that the change is enough to justify the claims or problems that can accompany such changes. Decision-making becomes more difficult in such a situation, and a decision to endorse or institute a new process, based on data from small samples, can be difficult [26].

Statistical methods are available to aid in the study of change. The fairly simple procedure called the "t-test" enables us to decide, to a selected degree of certainty, whether a statistically significant difference exists between one set of data and another (assuming that the populations are approximately normal) [27].

Because statistical tests are based on probability, there is some chance that the wrong conclusion is reached. The choice of the level of certainty defines that degree of chance that the wrong conclusion was reached. In Table 4-7, the use of a 95% level of certainty means that the original hypothesis--the pollutant concentration during normal operation is the same as that during waste firing--has only a 5% chance that it is incorrect.

It can be seen from Table 4-7 that particulate emissions levels between normal operation and waste firing were essentially identical. The apparent difference in emission levels for NO_x and total hydrocarbons do illustrate a deductive result due to the addition of waste firing to the kiln. Mean levels of CO in the stack gas were doubled when waste was burned, although this parameter was not given statistical treatment because statistical the averaging could not handle the excursions above 1,000 ppm CO. As waste is burned, the CO and THC levels rise, indicative of less complete combustion. If CO and THC increase, then NO_x levels should decrease, which does indeed occur.

4.4.9 Trace Elements in Particulate Matter

Selected samples of particulate matter were analyzed for trace element content. Since the waste fuels had negligible levels of trace metals, it was not expected that particulate dust would contain high levels of metals. In general, the metal content of the particulate matter is representative of cement dust. Results are tabulated in Table 4-8.

4.4.10 Process Water

Process water samples were taken during each test run from the water line near the slurry tanks. These samples represent "incoming" water to the plant, not plant discharges. The water is evaporated in the drying section of the cement kiln. A grab sample bottle was filled from the integrated water sampling vessel after mixing. The analysis conducted was GC/MS screening for organic priority pollutants, in particular, the three chlorinated compounds known to be present in the waste fuel. Table 4-9 presents the results of the volatile organic priority pollutant screening analysis. Of the three POHCs designated in the program, carbon tetrachloride was not detected in any water samples, chloroform was detected below the screening level for test runs W3-3 and W4-2, and methylene chloride was present in several water samples with up to 20 μg/L in test runs W3-1 and W3-2.

The "worst case" value of 20 μg/L of methylene chloride for run W3-1 adds some contribution to the W_{in} computation used to calculate DRE's. During run W3-1, the plant was feeding 65,300 kg/hr (72 ton/hr) of slurry containing 34.6% H_2O. This converts to a total water input of:

$$\frac{72\ \text{ton}}{\text{hr}} \times \frac{2{,}000\ \text{lb}}{\text{ton}} \times \frac{0.346\ \text{lb H}_2\text{O}}{\text{lb feed}} \times \frac{\text{gal}}{8.33\ \text{lb H}_2\text{O}} \times \frac{3.785\ \text{L}}{\text{gal}} = 22{,}639\ \text{L/hr}$$

TABLE 4-8. TRACE ELEMENT CONTENT OF PARTICULATE MATTER, μg/g

Element	Run number BW-2	Run number W1-1	Run number W3-2	Run number W4-2	Lab blank, μg/filter	Detection limit, μg
Be	2.9	2.4	2.8	4.0	<0.15	0.003
Cr	96.7	51.1	496.5	3,082	<3.5	0.070
Mn	195.4	1555.5	182.5	670.0	0.63	0.010
Pb	ND[a]	ND	ND	ND	<20.0	0.400
Ti	308.4	170.1	223.8	280.2	<1.45	0.029
Al	8,149	4,979	3,732	5,634	409	0.230
Ca	170,755	140,679	120,999	130,669	1,620	0.120
Cu	ND	ND	47.8	213.8	<7.5	0.150
Mo	206.4	168.2	209.5	590.4	<2.3	0.046
Sb	ND	ND	ND	ND	<43.0	0.860
V	33.6	48.9	186.1	240.8	<6.0	0.120
B	LLB[b]	LLB	LLB	LLB	311.0	0.150
Cd	ND	ND	5.7	23.3	<1.3	0.026
Fe	10,246	8,152	10,993	30,608	26.1	0.060
Na	12,146	LLB	LLB	6,693	7,630.0	0.095
Sn	ND	ND	ND	59.9	<32.5	0.650
Zn	LLB	64.6	91.4	327.7	27.2	0.050
Ba	LLB	LLB	LLB	LLB	31.0	0.007
CO	ND	ND	ND	63.9	<4.0	0.080
Mg	LLB	LLB	LLB	LLB	633.0	0.014
Ni	ND	ND	208.4	2,458	<10.0	0.200
Sr	100.1	91.9	75.2	77.0	1.71	0.013
K	34,564	33,728	52,004	44,366	359.0	6.500

[a] ND = none detected.

[b] LLB = less than laboratory blank.

The amount of methylene chloride in this water is:

$$\frac{20\ \mu g\ MeCl_2}{L\ H_2O} \times \frac{22,639\ L\ H_2O}{hr} \times \frac{g}{10^6\ \mu g} \times \frac{lb}{453.57\ g} = 0.001\ lb/hr\ MeCl_2$$

Therefore, the POHCs contained in the water used in the slurry feed can be neglected for all DRE calculations.

4.4.11 Kiln Baghouse Dust

Kiln baghouse dust was analyzed for potassium, sodium, and chlorine content. Results are presented in Table 4-10, and compared to typical values [28].

The baghouse dust was also submitted to an RCRA Extraction Procedure toxicity test to determine landfill suitablility. Two

TABLE 4-9. SUMMARY OF RESULTS OF PROCESS WATER SCREENING ANALYSIS FOR VOLATILE ORGANIC PRIORITY POLLUTANTS

Compound	Concentration, µg/L BW-1	BW-2	BW-3	W1-1	W2-1	BW-4	BW-SASS	W1-2	W3-1	W3-2	W3-3	W4-2	W4-3
Methylene chloride[a]	<10	0	0	0	<10	<10	<10	<10	20	20	10	0	0
Toluene	<10	<10	0	<10	0	0	<10	<10	0	10	<10	<10	<10
Ethylbenzene	0	0	0	0	0	0	0	0	0	0	0	0	0
1,1,1-Trichloroethane	0	0	0	0	<10	<10	0	0	<10	0	<10	<10	<10
Trichloroethylene	0	0	0	0	0	0	0	0	<10	<10	<10	<10	<10
Benzene	0	0	<10	<10	0	0	0	0	<10	<10	<10	<10	<10
Tetrachloroethylene	0	0	<10	0	<10	<10	<10	<10	<10	<10	<10	<10	<10
Chlorobenzene	0	0	0	<10	0	0	0	0	0	0	0	<10	0
Chloroform[a]	0	0	0	0	0	0	0	0	0	0	<10	<10	0
Dichlorobromomethane	0	0	0	0	0	0	0	0	0	0	<10	<10	0
Chlorodibromomethane	0	0	0	0	0	0	0	0	<10	0	<10	<10	0
Carbon tetrachloride[a]	0	0	0	0	0	0	0	0	0	0	0	0	0

Note: A "0" in the table signifies that the compound was not detected in the sample. A "<" in the table signifies that the level detected was less than the screening level.

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[a] POHC in waste fuel.

TABLE 4-10. ELEMENTAL ANALYSIS OF BAGHOUSE DUST FOR K, Na, AND Cl

Run number	Potassium, %	Sodium, %	Chlorine, %
BW-1	6.24	0.29	NA[a]
BW-SASS	3.65	0.39	NA
W1-1	6.51	0.57	NA
W2-1	5.58	1.22	NA
W3-SASS-1	4.42	0.54	NA
W3-2	6.80	0.58	NA
W4-1	5.00	0.49	0.36
W4-2	8.00	0.78	0.52
Typical value [28]	3.66[b]	0.96[b]	0.77[c]
Range[b,c]	0.34-23.2	0.05-2.77	0.1-12.3

[a] NA = not analyzed.

[b] Average of 113 dusts from 102 plants.

[c] Average of 57 plants.

liters of water containing up to 400 mL of 5N acetic acid were leached through 100 g of baghouse dust. The resulting leachate was then analyzed for trace element composition (Table 4-11) and GC/MS screened for organic priority pollutants (Table 4-12). It cannot be assumed that 100% recovery of any element or organic compound results; rather, it is a test designed to simulate the resulting leachate as it may be formed in a landfill environment.

Dust from cement kilns is not classified as a hazardous waste, based on EP toxicity test criteria. Of 113 samples taken from 102 domestic cement plants, only one in the research study [28] had a leachate concentration that exceeded any of the toxicity limits, also shown in Table 4-11. None of the San Juan Cement samples exceeded the limits.

4.5 DIOXIN AND DIBENZOFURAN TEST RESULTS

One of the objectives of the program was to ascertain the formation of chlorinated dioxins and chlorinated dibenzofurans as as products of combustion. Chlorinated dioxins and chlorinated dibenzofurans are among the most toxic substances to man. EPA officials and concerned citizens groups required that the demonstration program conduct extensive sampling and analysis for these compounds. During the course of the program, a total of 28 different samples were collected for analysis of chlorinated dioxins and chlorinated dibenzofurans. These samples included air emission samples and baghouse dust samples as shown below:

TABLE 4-11. TRACE ELEMENT CONCENTRATION IN LEACHATE FORMED IN EPA RCRA EXTRACTION PROCEDURE, µg/mL LEACHATE

Element	Maximum concentration allowed [29,30]	Run number								
		BW-2	BW-SASS	W1-1	W2-1	W3-SASS-1	W3-2	W4-1	W4-2	W4-4
Be	-	0.026	0.038	0.020	0.033	0.034	0.033	0.028	0.034	0.030
Cr	5.0	0.272	0.267	0.170	0.225	0.271	0.210	0.191	0.227	0.242
Mn	-	0.022	0.099	0.018	0.024	0.025	0.022	0.019	0.023	0.022
Pb	5.0	0.738	0.505	0.409	0.463	0.593	0.487	<0.400	0.538	0.525
Ti	-	0.096	0.120	0.073	0.109	0.120	0.101	0.082	0.108	0.107
Al	-	0.723	1.46	0.392	0.636	0.459	0.501	0.459	0.802	0.689
Ca	-	1,160.0	2,000.0	828.0	1,930.0	1,820.0	2,060.0	1,310.0	1,990.0	1,360.0
Cu	-	0.253	0.256	0.189	0.227	0.261	0.230	0.163	0.233	0.249
Mo	-	1.89	1.57	1.44	1.27	1.51	1.40	1.34	1.39	1.50
Sb	-	<0.860	<0.860	<0.860	<0.860	<0.860	<0.860	<0.860	<0.860	<0.860
V	-	<0.120	0.615	0.194	<0.120	<0.120	<0.120	<0.120	<0.120	0.130
B	-	0.727	0.795	0.555	0.702	1.10	0.705	0.600	0.697	0.672
Cd	1.0	0.038	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026
Fe	-	0.076	0.302	0.099	0.088	0.092	<0.060	<0.060	<0.060	0.065
Na	-	89.6	155.0	142.0	251.0	134.0	135.0	102.0	194.0	226.0
Sn	-	<0.650	<0.650	<0.650	<0.650	<0.650	<0.650	<0.650	<0.650	<0.650
Zn	-	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Ba	100.0	0.608	0.290	0.485	2.32	1.29	1.62	0.794	1.19	1.06
Co	-	0.096	0.097	<0.080	0.091	0.113	0.090	<0.080	0.097	0.102
Mg	-	<0.014	5.29	0.019	0.026	<0.014	<0.014	<0.014	<0.014	<0.014
Ni	-	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
Sr	-	1.16	0.331	0.511	0.730	0.905	0.694	0.638	0.732	0.638
K	-	2,080.0	1,080.0	1,430.0	1,050.0	1,020.0	1,620.0	1,230.0	1,940.0	2,350.0

TABLE 4-12. ORGANIC PRIORITY POLLUTANT CONCENTRATIONS IN LEACHATE FORMED IN EPA RCRA EXTRACTION PROCEDURE, μg/L LEACHATE FOR KILN DUST FROM RUN W4-2

Compound	Base/neutral extractable fraction	Acid extractable fraction
Naphthalene	<10	0
Isophorone	520	0
Phenol	0	40

Note: A '0' signifies that the compound was not detected. A'<' signifies that the compound was detected but less than the screening level indicated.

- 4 SASS train samples (particulates and vapors in stack gas)
- 5 EPA Method 5 samples (particulates in stack gas)
- 11 Baghouse dust samples (plant solid waste)
- 8 RCRA extracts of baghouse dust samples (plant solid waste).

Eight samples were taken during baseline (nonburning) conditions and 20 samples were taken during hazardous waste buring operations. The SASS train samples resulted in three sections for analysis: 1) methylene chloride rinses of the sampling probe, teflon line, filter holder, and organic module, 2) combined filter and XAD-2 absorbent resin, and 3) the condensate water removed from the organic module during sampling.

Quality control was carried out by spiking all samples with either $^{13}C_{12}$- labeled 2,3,7,8-tetrachlorodibenzo-p-dioxin ($^{13}C_{12}$-2,3,7,8-TCDD) and $^{37}Cl_4$- labeled 2,3,7,8-tetrachlorodibenzofuran ($^{37}Cl_4$-2,3,7,8-TCDF). In most cases the entire sample, whether a probe rinse or filter, was prepared. For the kiln dust 10 g samples were used which allowed replicates to be run and also some spiking experiments (with PCDDs) beyond the use of the labeled standards.

The results of the analysis of the SASS runs are given in Table 4-13 for PCDD's and Table 4-14 for PCDF's. Results are reported for tetrachloro- through octachloro- species. The last column of the tables is the average percent recovery of the labeled internal standard. Spike levels ranged from 5 to 45 ng per sample. In some cases low or high recoveries were observed. These can only

TABLE 4-13. SASS TRAIN EMISSION TEST RESULTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD's), ng/m³

Run no.	PCDD isomer					Average recovery[a], %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
BW-1B (field blank)	ND[b]	ND	ND	ND	ND	77
BW-1	ND	ND	ND	ND	ND	91
W3-1	ND	ND	ND	ND	ND	58
W4-4	ND	ND	ND	ND	ND	76
W6-1	ND	ND	ND	ND	ND	62
Average detection limit[c]	1.6	1.6	3.4	3.4	4.9	

[a] Calculated based on recovery of Carbon-13 labeled 2,3,7,8-TCDD and the average of recoveries for train rinse solvent, condensate water, and desorbed resin and filter.

[b] ND = Not detected.

[c] Calculated as lower limit of detection for entire SASS train and the average of all SASS run gas volumes.

TABLE 4-14. SASS TRAIN EMISSION TEST RESULTS FOR POLYCHLORINATED DIBENZOFURANS (PCDF's), ng/m³

Run no.	PCDF isomer					Average recovery[a], %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
BW-1B (field blank)	ND[b]	ND	ND	ND	ND	90
BW-1	ND	ND	1.35	0.74	ND	97
W3-1	ND	ND	ND	ND	ND	103
W4-4	ND	ND	ND	ND	ND	93
W6-1	ND	ND	ND	ND	ND	72
Average detection limit[c]	1.6	1.6	3.4	3.4	4.9	

[a] Calculated based on recovery of Chlorine-37 labeled 2,3,7,8-TCDD and the average of recoveries for train rinse solvent, condensate water, and desorbed resin and filter.

[ba] ND = Not detected.

[c] Calculated as lower limit of detection for entire SASS train and the average of all SASS run gas volumes.

be attributed to variations in the extraction process and variability in the analyses. The tables also list the average detection limits for the individual PCDD and PCDF isomers. The highest detection limits were observed for the methylene chloride rinse extracts since these were the most contaminated portions of the sample train and were subject to the greatest interferences.

The baseline SASS run (BW-SASS) showed some positive, detectable values of hexachloro- and heptachlorodibenzofuran in the absorbent resin extract, although none could be detected in the other portions of the train. This caused the reported value to be less than the average detection limit for the entire train. It is noteworthy that no PCDD's or PCDF's were detected in any waste burning SASS samples.

Tables 4-15 and 4-16 present the results of PCDD and PCDF emissions, respectively, based on the analysis of the particulate filters and probe rinses from selected EPA Method 5 runs. No detectable quantities of PCDD's were found in any of the particulate samples, and small quantities of pentachloro-, hexachloro-, and heptachloro-PCDF's were found in only one sample, run W3-3. These values detected ranged from 10% to 250% greater than the detection limit.

TABLE 4-15. EMISSION TEST RESULTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS BASED ON EPA METHOD 5 PARTICULATE ANALYSIS, ng/m^3

	PCDD isomer					
Run no.	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Recovery, %
BW-3	ND	ND	ND	ND	ND	104
W1-2	ND	ND	ND	ND	ND	48
W2-1	ND	ND	ND	ND	ND	103
W3-3	ND	ND	ND	ND	ND	84
W4-3	ND	ND	ND	ND	ND	68
Detection limit, ng/filter	5	5	10	10	15	

These detectable emissions occurred when the kiln was fed 2.75×10^{-4} m^3/s (4.35 gpm) of waste which contained 21.4% chlorine. This corresponds to a chlorine input of 3.5% of total fuel input (fuel oil plus hazardous waste) which results in the production of off-spec cement clinker and a potentially kiln-damaging condition. Section 4.7 describes how this is an operating condition which is intolerable for the cement plant. Thus, the generation of detectable quantities of PCDF's occurred only when operating an "upset" or "out-of-control" kiln. Under other conditions the cement process did not emit PCDF's, and did not emit PCDD's

TABLE 4-16. EMISSION TEST RESULTS FOR POLYCHLORINATED DIBENZOFURANS BASED ON EPA METHOD 5 PARTICULATE ANALYSIS, ng/m^3

Run no.	PCDF isomer					Recovery, %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
BW-3	ND	ND	ND	ND	ND	136
W1-2	ND	ND	ND	ND	ND	55
W2-1	ND	ND	ND	ND	ND	115
W3-3	ND	11.0	25.7	8.1	ND	112
W4-3	ND	ND	ND	ND	ND	98
Detection limit, ng/filter	5	5	10	10	15	

under any waste burning conditions. This lack of detectable quantities of PCDD and PCDF is an expected result because the waste fuel contains no polychlorophenolate precursors, the combustion temperatures were typically well above 1000°C, and a supplemental fuel was used to burn the wastes [31].

The baghouse dust and RCRA EP extract from the baghouse dust were also analyzed for the presence of PCDD's and PCDF's. No detectable quantities were found in any of the samples. Tables 4-17 through 4-20 present these results.

TABLE 4-17. ANALYSIS OF BAGHOUSE DUST FOR POLYCHLORINATED DIBENZO-p-DIOXINS, ng/g

Run no.	PCDD isomer					Recovery, %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
Na_2SO_4 blank	ND[a]	ND	ND	ND	ND	94
BW-1	ND	ND	ND	ND	ND	57
BW-2	ND	ND	ND	ND	ND	90
BW-3	ND	ND	ND	ND	ND	74
W1-1	ND	ND	ND	ND	ND	81
W2-1	ND	ND	ND	ND	ND	66
BW-SASS	ND	ND	ND	ND	ND	36
W3-1	ND	ND	ND	ND	ND	98
W3-2	ND	ND	ND	ND	ND	57
W4-1	ND	ND	ND	ND	ND	55
W4-2	ND	ND	ND	ND	ND	78
W4-2 replicate	ND	ND	ND	ND	ND	84
Spike level	9	19	32	18	38	-
W4-2 spiked	6.2	17	31	15	12	86
Recovery, %	69	89	97	83	32	-
Detection limit	1	1	2	2	5	-

[a] ND = Not detected.

TABLE 4-18. ANALYSIS OF BAGHOUSE DUST FOR POLYCHLORINATED DIBENZOFURANS, ng/g

Run no.	PCDF isomer					Recovery, %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
Na_2SO_4 blank	ND[a]	ND	ND	ND	ND	78
BW-1	ND	ND	ND	ND	ND	89
BW-2	ND	ND	ND	ND	ND	101
BW-3	ND	ND	ND	ND	ND	77
W1-1	ND	ND	ND	ND	ND	123
W2-1	ND	ND	ND	ND	ND	79
BW-SASS	ND	ND	ND	ND	ND	70
W3-1	ND	ND	ND	ND	ND	88
W3-2	ND	ND	ND	ND	ND	76
W4-1	ND	ND	ND	ND	ND	71
W4-2	ND	ND	ND	ND	ND	75
W4-2 replicate	ND	ND	ND	ND	ND	83
Detection limit	1	1	2	2	5	

[a] ND = Not detected.

TABLE 4-19. ANALYSIS FOR POLYCHLORINATED DIBENZO-p-DIOXINS IN RCRA EXTRACT OF BAGHOUSE DUST, ng/total extract

Run no.	PCDD isomer					Recovery, %
	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	
BW-SASS	ND[a]	ND	ND	ND	ND	61
W2-1	ND	ND	ND	ND	ND	73
W3-1	ND	ND	ND	ND	ND	66
W3-2	ND	ND	ND	ND	ND	49
W4-1	ND	ND	ND	ND	ND	79
W4-2	ND	ND	ND	ND	ND	69
W4-4	ND	ND	ND	ND	ND	71
W6-1	ND	ND	ND	ND	ND	84
Detection limit	5	5	10	10	15	

[a] ND = Not detected.

TABLE 4-20. ANALYSIS FOR POLYCHLORINATED DIBENZOFURANS IN RCRA EXTRACT OF BAGHOUSE DUST, ng/total extract

Run no.	PCDF isomer Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Recovery, %
BW-SASS	ND[a]	ND	ND	ND	ND	121
W2-1	ND	ND	ND	ND	ND	109
W3-1	ND	ND	ND	ND	ND	112
W3-2	ND	ND	ND	ND	ND	94
W4-1	ND	ND	ND	ND	ND	90
W4-2	ND	ND	ND	ND	ND	122
W4-4	ND	ND	ND	ND	ND	100
W6-1	ND	ND	ND	ND	ND	108
Detection limit	5	5	10	10	15	

[a] ND = Not detected.

4.6 AMBIENT AIR TEST RESULTS

The computer modeling and siting of the ambient air particulate monitoring stations was discussed in Section 3.5. Samples were collected at "upwind" (Station I) and "downwind" (Station II) locations based on seasonal and monthly wind patterns, which remain quite steady due to the proximity of the coast and prevalent trade winds. The ambient air particulate matter concentrations found at both stations are summarized in Tables 4-21 and 4-22. Also tabulated are parameters of interest to be considered together with the results.

The sampling periods were representative of a 24-hr sample as recommended by the U.S. EPA method (40 CRF 50), Appendix B. Samples taken on December 12 at Station No. I and on December 8 and 10 at Station No. II depart somewhat from this standard but still were considered valid for the study purpose. Sample #066 ran for 46 hours or two, 24-hour periods which was considered valid since the two periods were consecutive and uninterrupted. (Samples could not be collected on due date because of floods in the study area.) Electrical power failure affected the total sampling time of samples #C-16 and #063. Sample #C-16 was considered valid since total sampling time was in excess of 90% of the total possible sampling time (1,380 min). Sample #063 was also considered valid although the sampler ran for only 70% of the time, since the emission source object of the study operates 24 hours a day.

The average concentration at the upwind station was 34.9 ± 5.5 (95% confidence limits) $\mu g/m^3$ of particulate matter; the average particulate concentration at the downwind station was 42.2 ± 7.7 $\mu g/m^3$. For comparison, the national primary ambient air quality standard

TABLE 4-21. AMBIENT AIR QUALITY CONCENTRATIONS AND SUMMARY OF SAMPLING DATA AROUND THE SAN JUAN CEMENT PLANT

Station No. I
VisiFloat #000EB

Starting day, 1981	Time per station, min	VisiFloat reading average	Flow rate, m^3/min	Volume sampled, $m^3 \times 10^3$	Filter no. per station	Particulates collected, mg	Ambient conc., µg/m^3
10/21	1,380	54	1.4725	2.0321	C-3	71.0	34.94
11/16(W1-2)	1,380	55	1.4913	2.0579	C-1	74.0	35.96
11/17	1,380	55	1.4913	2.0579	C-6	107.0	52.0
11/18	1,380	55	1.4913	2.0579	C-7	67.0	32.56
11/19	1,380	55	1.4913	2.0579	C-8	73.0	35.47
12/2	1,380	55	1.4913	2.0579	C-9	53.0	25.75
12/3(W3-1)	1,380	55	1.4913	2.0579	C-11	62.0	30.13
12/7	1,380	55	1.4913	2.0579	C-13	40.0	19.44
12/8(W4-1)	1,380	55	1.4913	2.0579	C-15	52.0	25.27
12/9(W4-2)	1,380	55	1.4913	2.0579	C-60	114.0	55.40
12/10(W4-3)	1,380	55	1.4913	2.0579	062	77.0	37.42
12/11	1,380	55	1.4913	2.0579	064	73.0	35.47
12/12	2,760	55	1.4913	4.1160	066	126.0	30.61
12/15	1,380	55	1.4913	2.0579	067	78	37.9

Average: 34.88
Maximum Concentration: 55.4
Date: 12/9/81
Minimum Concentration: 19.44
Date: 12/7/81

TABLE 4-22. AMBIENT AIR QUALITY CONCENTRATIONS AND SUMMARY OF SAMPLING DATA AROUND THE SAN JUAN CEMENT PLANT

Station No. II
VisiFloat #11800

Starting day, 1981	Time per station, min	VisiFloat reading average	Flow rate, m^3/min	Volume sampled, $m^3 \times 10^3$	Filter no. per station	Particulates collected, mg	Ambient conc., $\mu g/m^3$
10/21	1,380	52	1.5250	2.1045	C-5	132.0	62.72
10/13	1,380	51	1.5100	2.0838	C-4	117.0	56.15
10/21	1,380	52	1.5250	2.1045	C-2	81.0	38.49
11/16(W1-2)	1,380	52	1.5250	2.1045	B-3	100.0	47.52
11/17	1,380	52	1.5250	2.1045	B-4	115.0	54.65
11/18	1,380	52	1.5250	2.1045	B-5	112.0	53.22
11/19	1,380	52	1.5250	2.1045	B-6	67.00	31.84
12/2	1,380	52	1.5250	2.1045	C-10	92.00	43.72
12/3(W3-1)	1,380	52	1.5250	2.1045	C-12	95.0	45.14
12/7	1,380	52	1.5250	2.1045	C-14	53.0	25.19
12/8(W4-1)	1,380	52	1.5250	1.9215	C-16	54.0	28.10
12/9(W4-2)	1,380	52	1.5250	2.1045	061	104.0	49.42
12/10(W4-3)	960	52	1.5250	1.4640	063	56.0	38.25
12/11	1,380	52	1.5250	2.1045	065	33.0	15.68

Average: 42.15
Maximum Concentration: 62.72
Date: 10/21/82
Minimum Concentration: 15.68
Date: 12/11/81

(NAAQS), which defines a level of air quality necessary to protect public health with an adequate margin of safety, is 260 μg/m^3 (24-hr) and 75 μg/m^3 (annual geometric mean).

As could be verified from the results, one station (No. I) was positioned to determine upwind or "background levels" of suspended particulate matter while the other station (No. II) was oriented downwind from the emissions of the San Juan Cement Company.

While no clear distinction can be made as to the specific contribution of the emissions from Kiln No. 2 to the total concentration observed at Station II, an average concentration difference of about 7.3 μg/m^3 was found at the downwind station. It may be concluded that the higher concentrations detected at Station II were caused, in the first instance, by the San Juan Cement emissions and, secondly, by dust re-entrainment and combustion emissions produced by the vehicular movement along Road No. 679. This 7.3 μg/m^3 difference is not statistically significant.

Moreover, there is no statistically significant difference between the waste burning days and the normal operation days at each station. Table 4-23 summarizes these data.

TABLE 4-23. COMPARISON OF AMBIENT PARTICULATE LEVELS ASSOCIATED WITH WASTE BURNING AROUND SAN JUAN CEMENT PLANT

Condition	Concentration, μg/m^3 Upwind	Concentration, μg/m^3 Downwind
Normal operation (n=9)	33.8 ± 6.9	42.4 ± 12.2
Waste burning (n=5)	36.8 ± 14.2	41.7 ± 10.8

Low particulate matter concentrations shown in Tables 4-21 and 4-22 were directly related to the weather conditions prevailing in the study area. Wind direction and speed and precipitation are the climatological parameters having the greatest influence in ambient air samples. In 24-hr samples, wind influence tends to be averaged out since direction and/or speed are seldom maintained for more than six hours in any one day. Precipitation, on the other hand, "washes-out" dust from the atmosphere, causing lower suspended particulate matter concentration. A summary of the wind and precipitation data during the study period as obtained from the National Climatic Center, NOAA, is listed in Tables 4-24 and 4-25. As an example of the aforementioned influence, notice that on October 12, 1981, when the wind was blowing from the east at an average speed of 3.04 m/s (6.8 mph) and with no precipitation recorded, Station II registered the highest concentration

TABLE 4-24. WEATHER DATA AT SAN JUAN CEMENT
DURING THE STUDY PERIOD

Date, 1981	Temperature, °C (°F) Maximum	Temperature, °C (°F) Minimum	Precipitation, mm (inches)
10/12	29 (85)	21 (70)	0 (0.0)
10/13	31 (87)	21 (70)	0 (0.0)
10/14	31 (87)	22 (72)	0 (0.0)
10/21	32 (90)	22 (71)	0.25 (0.01)
10/22	31 (88)	21 (70)	0 (0.0)
11/16	32 (89)	22 (72)	0 (0.0)
11/17	31 (88)	24 (75)	0 (0.0)
11/18	32 (89)	24 (76)	0 (0.0)
11/19	31 (88)	24 (76)	16.5 (0.65)
11/20	31 (87)	24 (76)	0 (0.0)
12/2	29 (84)	21 (69)	0 (0.0)
12/3	29 (84)	21 (69)	0.76 (0.03)
12/4	29 (84)	22 (71)	0 (0.0)
12/7	27 (80)	21 (69)	3.8 (0.15)
12/8	29 (84)	21 (70)	0 (0.0)
12/9	31 (88)	20 (68)	0 (0.0)
12/10	31 (88)	21 (69)	23.9 (0.94)
12/11	30 (86)	20 (68)	15.5 (0.61)
12/12	26 (78)	22 (71)	248.9 (9.8) 25.4
12/13	25 (77)	21 (70)	229.9 (9.05)
12/14	27 (80)	22 (71)	127.0 (5.0)
12/15	25 (77)	22 (71)	0 (0.0)
12/16	29 (84)	21 (70)	1.0 (0.04)

during the study period; 62.72 μg/m³. In contrast, the next day, October 13, 1981, when the wind shifted to a southwest direction, the recorded concentration was lower.

The impact of precipitation can also be observed on the October 21 sample and the period of December 10-14, 1981, when a total of 645.2 mm (25.4 in.) of rain was recorded. The recorded particulate concentrations during this period were very low.

The samples collected during the month of October are to be considered as background with respect to the demonstration project, which did not get underway until October 29. By reviewing these data it can be concluded that no specific influence can be detected in the levels of concentration at background and when the project was being conducted.

The average levels recorded at each station could be classified as representative of suburban areas. The average value of 40 μg/m³ is commonly used as the typical or average background level for particulate matter in similar studies. Table 4-26 summarizes

TABLE 4-25. WIND DATA AT THE ISLA VERDE INTERNATIONAL AIRPORT (SAN JUAN) DURING THE STUDY PERIOD, INCLUDING AVERAGE TEMPERATURE

Date, 1981	Average temperature, °C (°F)	Wind Velocity, m/s (mph)	Wind Direction, card.
10/12	30 (86)	7.6 (17)	E
10/13	29 (85)	7.2 (16)	SW
10/14	31 (87)	6.7 (15)	SW
10/21	28 (82)	7.2 (16)	SW
10/22	27 (80)	9.8 (22)	S
11/16	27 (80)	8.9 (20)	E
11/17	28 (82)	7.6 (17)	E
11/18	28 (82)	7.6 (17)	E
11/19	28 (82)	6.7 (15)	E
11/20	28 (82)	8.0 (18)	E
12/2	27 (80)	8.9 (20)	E
12/3	27 (80)	7.6 (17)	E
12/4	27 (80)	8.0 (18)	E
12/7	26 (78)	7.2 (16)	E
12/8	28 (82)	6.7 (15)	E
12/9	28 (82)	6.7 (15)	S
12/10	29 (84)	6.7 (15)	NW
12/11	24 (75)	11.6 (26)	NW
12/12	24 (75)	8.9 (20)	E
12/13	26 (79)	9.8 (22)	E
12/14	24 (76)	13.0 (29)	E
12/15	27 (81)	8.0 (18)	E
12/16	27 (80)	7.6 (17)	E

values found at stations located in suburban areas near U.S. cities considered comparable in population to the suburban communities included in the study area.

The color of the samples collected, a light to a semi-dense grayish-brown, makes us conclude that the particulate matter collected is mainly soil and combustion products normally found in community air. Contribution from San Juan Cement emissions may be inferred, but its contribution is not clearly detected.

4.7 OPERATIONAL EXPERIENCE

Key observations made during the operation of San Juan Cement's kiln #2 are presented in this section. A synopsis of how these objectives influenced the experimental design is needed before the operational experience can be appreciated.

TABLE 4-26. SUSPENDED PARTICULATES AMBIENT AIR ANNUAL AVERAGE CONCENTRATION FOR SELECTED CITIES OF THE U.S. (NAAQS = 75 $\mu g/m^3$)

State	City	Annual average concentration, $\mu g/m^3$
Alabama	Phoenix City	55
	Selma	52
California	Azusa	126
	Pittsburg	61
Florida	Lake Worth	36
South Carolina	Florence	54
Texas	Nacogdoches	38
West Virginia	Clarksburg	78
Arkansas	El Dorado	151
Michigan	Monroe	76
	Trenton	77

Air Quality Data-1975 Annual Statistics, US-EPA, Research Triangle Park, North Carolina 27711 (EPA 450/2-77-002)

San Juan Cement's objective is to produce and to continue to produce cement at a profit through the production of saleable cement product. Burning of hazardous wastes as a fuel is an incidental, but a potentially profitable and potentially environmentally desireable part of their corporate objective. The demonstration program was conducted to yield saleable cement product, to safeguard the capital investment in the kiln, to maintain long term cement kiln operating reliability, and to train kiln operators to properly burn hazardous waste as fuel. All of these objectives were met.

The EQB 's objective is to ensure that incineration of hazardous wastes does not degrade the environment; thus, ensuring that this hazardous waste disposal technique has a net positive impact on the total environment. The demonstration program was conducted under a temporary operating permit which specified that pesticides, herbicides, or polychlorobiphenyls (PCBs) would not be burned. The permit also specified that organic solvent emissions would not exceed 3 pounds per hour or 15 pounds per day. It also specified that stack sampling would be conducted during all burning tests and that a burn would be terminated if the requirements of the permit were exceeded. The waste feeding system was to be rendered inoperable at the conclusion of the demonstration program. All of these objectives (requirements) were met.

Operational experience was as follows:

1. The start-up, operating, and shut-down procedures written by the production foreman for the kiln operators provide for stable kiln operations and yield excellent manifest information on the quantities of wastes burned. At the end of the demonstration program, cement kiln operators were able to start-up the hazardous waste burning with no apparent effect on kiln operation. During emergency situations such as pump failures or line weld breaks, operators were able to shut down the hazardous waste burning without upsetting cement kiln operation.

2. The most important factor in maintaining a stable kiln operation was to maintain a constant total heat input to the kiln. The addition of 2.929×10^6 W (10 million Btu/hr) of hazardous waste must be offset by the equivalent thermal reduction in fuel oil. Overcorrection or undercorrection will result in an oscillating burning zone temperature which will require 2 to 4 hours to stabilize. Maintenance of the proper heat balance will result in no observable burning zone changes when hazardous waste burning is either started or stopped.

3. The cement kiln will remain in a stable and controlled operating condition when the chlorine content of the total fuel (fuel oil plus hazardous waste) is 3% (by weight) or less. When chlorine content exceeds 3%, the kiln becomes operationally unstable about 90 minutes after the start of burning more than 3% chlorine in the total fuel. The instability takes several forms. The burning zone temperature drops from 1430°C (2,600°F) to below 815°C (1,500°F) in less than two minutes some 80 to 90 minutes into the burn. The kiln starts a rapid loss of refractory lining (coating) to cement clinker product. A clinker ring forms in the burning zone. Hydrocarbon emissions increase (about fourfold) in the stack. Recovery from this upset condition is achieved by shutting off the hazardous waste while maintaining a constant heat balance. Remarkably, the kiln recovers in 12 to 15 minutes if the waste is shut off as soon as kiln goes into an upset condition. Continued operation during an upset would destroy the kiln. It is presumed that the excess chlorine is absorbed in the lining and reduces its slagging temperature to below 815°C (1,500°F). When the lining starts to slag, all heat goes to melt the lining, not to making cement. It is presumed that the kiln recovers in about 15 minutes because it takes the burning zone about 15 minutes to purge itself of slagged lining. Recovery is as dramatic as is the upset.

4. Even though the cement kiln remains stable up to about 3% chlorine in the total fuel, the product quality becomes unacceptable when the chlorine content exceeds 1% of the total fuel at San Juan Cement. There is no change in stack emissions of criteria pollutants when the chlorine content is 1% of total fuel versus baseline (nonwaste burning) conditions. The cement product quality degrades to unsaleable material before any changes in environmental acceptability are observed. Conversely, production of acceptable product should yield an acceptable environment.

5. Clinker rings can be formed by either temperature excursions in the burning zone when not burning hazardous waste or by excessive chlorine additions to the kiln. Operators at San Juan Cement were successful at breaking clinker rings simultaneous with burning chlorinated hazardous waste. It was not required to cease hazardous waste burning to break a clinker ring.

6. The key process control indicators to maintain stable kiln operations during hazardous waste burning are chain gate temperature and burning zone temperature. These parameters provide the earliest accurate warning of impending upset conditions. Stack gas concentrations of oxygen and carbon monoxide do not correlate with hazardous waste burning performance in cement kilns.[a] Variations in percent oxygen and part per million carbon monoxide are more indicative of air infiltration to the kiln and the kiln's heat balance changes than to incineration in the burning zone of the kiln.

7. The generic nozzle design for hazardous waste injection into cement kilns should not imitate the nozzle design for the fuel oil injection. The preferred design should inject the waste as a well-atomized liquid stream. Atomization of the waste will improve waste combustion but it should not modify the flame shape and profile such that hot spots in the refractory lining would form; thus destroying kiln integrity.

8. Burning of hazardous waste in cement kilns serves as a fuel oil igniter when fuel oil preheat temperatures fall below 115°C (240°F). During one burn, the plant's boiler house temporarily lost steam pressure and the fuel oil preheat fell to 60°C (140°F). Burning only the fuel oil

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[a] This conclusion infers nothing about their use in hazardous waste incinerators. It applies only to cement kilns burning hazardous waste.

at this preheat temperature resulted in a sooty flame and increased stack hydrocarbon emissions. Injection of hazardous waste ignited the fuel oil, stopped the sooty flame and reduced hydrocarbon emissions. Plant personnel were able to exploit the waste's lower flash point and compensate for loss of preheat steam pressure.

9. The preferred materials of construction for the hazardous waste storage and feeding system include carbon steel, black iron and bronze. Brass and aluminum are not to be used. Stainless steel (304) is not as good as black iron due to chlorine stress corrosion. Type 316L stainless steel may be acceptable.

Recommended design and operational criteria for a full-scale facility are provided in Appendix B of this report. They represent an integrated approach to good engineering practice as it relates to environmental and product acceptability.

SECTION 5

POHCs, PICs, AND CHLORINE MATERIAL BALANCE RESULTS

The complex combustion chemistry for organic materials becomes perplexing when a broad range of organic compounds present in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO_2 in the combustion process, but trace amounts of organic chemicals survive the oxidation process and are only partially reacted. In addition, small amounts of other organic chemicals may be produced if proper conditions exist. Oxidative chemical principles would suggest that all organic compounds regardless of their origin would be converted to CO_2 and other primary products if a sufficiently high temperature is achieved in the presence of adequate oxygen for a time long enough for complete oxidation to occur. If the conditions of temperature, time, and oxygen are not met, the combustion of the organic material in the fuel, plus any new organic components formed in the combustion process, would be expected to be incomplete and some possibly detrimental compounds of concern may then appear in the effluents [31]. Accordingly, this demonstration program investigated the amount of destruction of the organic compounds in the waste (DRE of the POHC's) and the types of organic compounds formed (PIC's).

Destruction and removal efficiency (DRE) for an incineration/air pollution control system is defined by the following equation:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} (100\%) \qquad (17)$$

where DRE = destruction and removal efficiency, %
W_{in} = mass feed rate of the principal organic hazardous constituent(s) to the incinerator
W_{out} = mass emission rate of the principal organic hazardous constituent(s) to the atmosphere (as measured in the stack prior to discharge).

Thus, DRE calculations are based on the combined efficiencies of destruction in the incinerator, or cement kiln, and removal from the gas stream in the air pollution control system. The (potential) presence of principal organic hazardous constituents in an incinerator's bottom ash (in this case, the cement clinker) or solid/liquid discharges from air pollution control devices is not accounted for in the DRE calculation as currently defined by the EPA. At San Juan Cement the air pollution control device is a fabric filter baghouse which is effective for collecting particulate matter but would not be an efficient control device for gaseous pollutants, particularly chlorinated hydrocarbons.

Destruction and removal efficiencies are normally measured only during trial burns and occasional compliance tests, and are used as a basis for determining whether or not the incinerator/air pollution control system operating conditions are adequate. Part 264, Subpart O regulations for hazardous waste incineration require a DRE of 99.99% for all principal organic hazardous components of a waste unless it can be demonstrated that a higher or lower DRE is more appropriate based on human health criteria. Specification of the principal organic hazardous constituents in a waste is subject to best engineering judgment, considering the toxicity, thermal stability, and quantity of each organic waste constituent. DRE requirements in the Subpart O regulations do not apply to metals or other noncombustible materials.

5.1 PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS

The principal organic hazardous constituents (POHCs) chosen in this demonstration program were the three chlorinated compounds known to be present in the waste fuel mixture:

(1) Methylene chloride (dichloromethane), CH_2Cl_2
(2) Chloroform (trichloromethane), $CHCl_3$
(3) Carbon tetrachloride, CCl_4

Within the family of chlorinated hydrocarbons, the monocarbon compounds are among the most difficult to destroy thermally. The carbon-chlorine bond is especially tenacious and, in general, the more C-Cl bonds present, the more difficult a compound will be to destroy. Accordingly, a monocarbon chlorine-containing molecule will tend to be harder to thermally destroy than a two carbon chlorine-containing molecule. The Gibbs free energy of formation values [32] at 1600°C (2421°F) illustrate this, where the amount of energy required to form a molecule (conversely, the "difficulty" required to destroy) can be expressed as:

$$CCl_4 > CHCl_3 > CH_2Cl_2 > C_2H_3Cl_3$$

These three POHCs were measured by gas chromatography with an electron capture detector via integrated bag samples collected from the kiln/baghouse exhaust stack (see Section 3 for detailed description).

Concentrations of the POHCs were measured during baseline testing (days when no waste fuel was burned) in order to give background or normal concentrations of the POHCs in the exhaust gas. The average background level was then subtracted from the results obtained during a waste fuel burn to arrive at the contribution attributable to the waste burn.

In order to convert the ppb expression of exhaust gas analysis results to $\mu g/m^3$, the following equation is used:

$$C(\mu g/m^3) = C(ppb) \times \frac{MW}{24.04} \times \frac{P}{760} \times \frac{298}{T + 273} \qquad (18)$$

where MW = molecular weight of compound, g/mol
24.04 = molar volume at 20°C and 760 mm Hg, L/mol
P = pressure of air sampled, mm Hg
T = temperature of air sampled, °C

Table 5-1 presents the calculation results which determine W_{out}, the mass emission rate, for the POHCs. The baseline concentrations are shown and the mass emission rates for the test runs have been corrected. The baseline data used are those taken from November 11, 12, and 18. Other baseline runs for chlorinated compounds which were made the day following a waste burn test have shown exhaust gas levels equal to or exceeding the levels seen during a waste burn. This phenomenon is, as yet, unexplainable.

TABLE 5-1. CORRECTED MASS EMISSION RATES OF POHCs

Run number	CH_2Cl_2, g/hr	$CHCl_3$, g/hr	CCl_4, g/hr
Baseline average, $\mu g/m^3$	46	374	2361
W1-1	-[a]	-[a]	-[a]
W1-2	<7.89	<22.2	78.0
W2-1	12.2	<19.0	<0.5
W3-1	<6.62	26.2	917.1
W3-2	53.1	28.0	580.1
W3-3	535.7	<19.9	225.4
W4-1	1124.9	448.1	1433.7
W4-2	369.2	167.8	1180.2
W4-3	678.1	449.9	1070.0
W4-4	9.71	317.0	194.1
W4-5	771.5	28.9	1069.5
W6-1	279.4	-[b]	-[b]
W5-1	556.5	495.3	298.4
W5-2	346.1	1451.0	418.2
W4/6-1	134.7	475.8	1185.2
W4/6-2	285.3	1303.1	209.1
W4/6-3	89.8	51.7	406.9
W4/6-4	323.4	<19.0	1040.9
W4/6-5	482.6	440.9	1362.1

[a] No measurements made during this run.

[b] Not present in waste fuel.

The calculations of the mass feed rates of the POHCs are presented in Table 5-2. This is a straightforward conversion of the calibrated volumetric flow rate of the waste fuel to the kiln times the volumetric percent of the POHC as determined by $(GC)^2$/MS or GC/EC analysis times the density at 25°C of the POHC. An example calculation is provided in Appendix A.

TABLE 5-2. MASS FEED RATE OF POHCs

Run number	CH_2Cl_2, kg/hr	$CHCl_3$, kg/hr	CCl_4, kg/hr
W1-1[a]	220.55	10.11	8.69
W1-2	282.29	17.52	15.06
W2-1[b]	254.60	13.47	10.86
W3-1	73.04	23.14	10.24
W3-2	131.97	41.28	18.50
W3-3	157.28	49.83	22.04
W4-1	63.80	31.83	63.22
W4-2	63.44	31.65	62.86
W4-3	125.78	62.75	124.64
W4-4	61.98	30.92	61.42
W4-5	115.94	57.85	114.88
W6-1	35.95	0.90	0.11
W5-1	8.30	29.80	66.67
W5-2	10.36	37.19	83.23
W4/6-1	56.06	10.85	20.18
W4/6-2	85.96	16.64	30.94
W4/6-3	20.60	3.94	7.42
W4/6-4	37.33	7.23	13.44
W4/6-5	91.69	17.75	33.01

[a] Flowrate not measure. Estimated to be 1.89 x 10^{-4} m^3/s (3 gpm).

[b] Flowrate not measured. Estimated to be 3.16 x 10^{-4} m^3/s (5 gpm).

The average DRE for each test run for the POHC's is presented in Table 5-3. Methylene chloride was destroyed to at least 99.0% efficiency, with the only exceptions being the two tests with waste batch #5 which contained only 1.4% methylene chloride. In general, the lower the mass feed rate of a POHC, the lower the DRE was.

Chloroform and carbon tetrachloride were more difficult to destroy than methylene chloride. Also, in most waste batches, methylene chloride was the largest POHC in the waste. Waste batches #4 and #5 had the largest amounts of chloroform and carbon tetrachloride, and the best DRE results for carbon tetrachloride were observed for the test runs on these two batches. Figure 5-1 illustrates

TABLE 5-3. DESTRUCTION AND REMOVAL EFFICIENCIES OF POHCs FOR DEMONSTRATION BURN TESTS AT SAN JUAN CEMENT COMPANY KILN #2, PERCENT

Run number	CH_2Cl_2	$CHCl_3$	CCl_4
W1-2[a]	>99.997	>99.842	99.309
W2-1[a]	99.995	>99.859	>99.996
W3-1	>99.991	99.887	91.043
W3-2	99.960	99.932	96.864
W3-3	99.659	>99.960	98.977
W4-1	98.237	98.592	97.732
W4-2	99.418	99.470	98.122
W4-3	99.461	99.283	99.142
W4-4	99.984	98.975	99.684
W4-5[c]	99.335	99.950	99.069
W5-1[c]	93.292	98.388	99.553
W5-2[c]	96.663	96.099	99.460
W6-1	99.223	-[b]	-[b]
W4/6-1[c]	99.760	95.617	94.129
W4/6-2[c]	99.668	92.171	99.325
W4/6-3[c]	99.564	98.703	94.512
W4/6-4[c]	99.133	>99.737	92.253
W4/6-5[c]	99.474	97.515	95.873

[a] Waste feed rate was estimated.

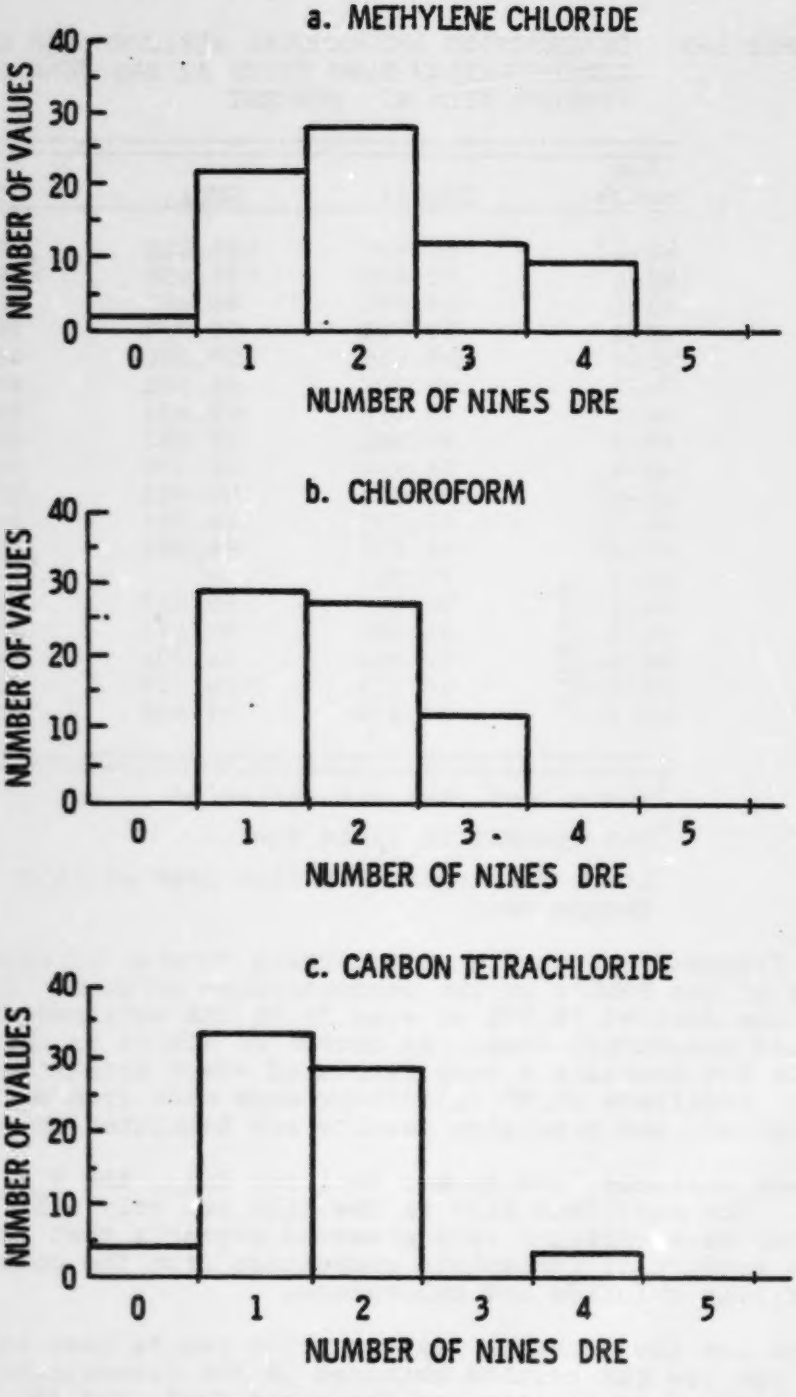
[b] Not present in waste fuel

[c] Stack gas volumetric flow rate of 1619 dscmpm used.

the frequency of obtaining a certain "number of nines" of DRE for each of the POHC's in the demonstration program. In few instances was the desired 99.99% or even 99.9% DRE obtained for the chlorinated monocarbon compounds chosen as POHC's in this program. Table 5-4 contains a compilation of every integrated bag sample run. Replicate GC/EC injections were made from each bag sample collected, and precision results are tabulated in Section 8.

In one instance, run number W6-1 for CCl_4, the W_{out} exceeded the W_{in}. The mass feed rate to the kiln was only 0.11 kg/hr, and the higher mass emission rate observed suggests that CCl_4 is formed as a product of incomplete combustion from the combustion of methylene chloride and chloroform.

There are two probable reasons which can be used as explanations for the low DRE results obtained in the demonstration program: (1) lack of atomization of the waste fuel, and (2) difficulty of incinerability of highly chlorinated monocarbon compounds.



a. METHYLENE CHLORIDE

b. CHLOROFORM

c. CARBON TETRACHLORIDE

Figure 5-1. Distribution of DRE results for each POHC.

TABLE 5-4. COMPILATION OF DRE's FOR ALL POHC's

Date	Bag collection time	Run number	Corrected stack gas concentration[a], ppb			Destruction and removal efficiency, %		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
11/11/81 11/12/81 11/18/81	Baseline background average concentration		13	75	369	-	-	-
11/16/81	1050-1130	W1-2A	ND	ND	ND	99.997[b]	99.842[c]	99.995[d]
	1205-1210	W1-2B	ND	ND	197	99.997[b]	99.842[c]	98.755
	1305-1410	W1-2C	ND	ND	174	99.997[b]	99.842[c]	98.900
	1425-1500	W1-2D	ND	ND	173	99.997[b]	99.842[c]	98.907
	1525-1610	W1-2E	ND	ND	ND	99.997[b]	99.842[c]	99.995[d]
	Average	W1-2	ND	ND	109	99.997[b]	99.842[c]	99.309
11/10/81	1400-1430	W2-1	36	ND	ND	99.995	99.859[c]	99.996[d]
12/03/81	1000-1130	W3-1A	ND	ND	2542	99.991[b]	99.919[c]	85.059
	1130-1240	W3-1B	ND	87	2030	99.991[b]	99.824	88.069
	1300-1530	W3-1C	ND	ND	ND	99.991[b]	99.919[c]	99.999[d]
	Average	W3-1	ND	56	1524	99.991[b]	99.887	91.043
12/04/81	0900-0930	W3-2A	105	ND	760	99.971	99.951[c]	97.304
	0940-1045	W3-2B	186	69	1007	99.949	99.915	96.427
	Average	W3-2	146	55	884	99.960	99.932	96.864
12/04/81	1415-1530	W3-3A	1746	ND	657	99.607	99.960[c]	98.090
	1540-1640	W3-3B	1282	ND	47	99.712	99.960[c]	98.863
	Average	W3-3	1514	ND	352	99.659	99.960[c]	98.977

(continued)

TABLE 5-4 (continued)

Date	Bag collection time	Run number	Corrected stack gas concentration[a], ppb			Destruction and removal efficiency, %		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
12/08/81	1420-1440	W4-1A	3857	1367	2012	97.737	97.740	97.842
	1445-1500	W4-1B	3182	1411	2762	98.133	97.668	97.038
	1505-1540	W4-1C	2764	128	2077	98.376	99.788	97.773
	1545-1555	W4-1D	2623	527	1872	98.432	99.129	97.993
	1600-1624	W4-1E	2599	827	1851	98.475	98.633	98.015
	Average	W4-1	3005	852	211	98.237	98.592	97.732
12/09/81	0912-0935	W4-2A	771	190	1507	99.545	99.684	98.375
	0935-1015	W4-2B	2022	296	978	98.807	99.510	98.945
	1030-1115	W4-2C	298	1231	1358	99.824	97.954	98.535
	1145-1220	W4-2D	2208	399	1511	98.697	99.337	98.370
	1230-1350	W4-2E	1201	ND	2939	99.291	99.934[c]	96.830
	1415-1440	W4-2F	380	ND	1895	99.776	99.934[c]	97.956
	1450-1515	W4-2G	ND	ND	2002	99.988[b]	99.934[c]	97.841
	Average	W4-2	986	319	1741	99.418	99.470	98.122
12/10/81	1230-1300	W4-3A	329	1223	1557	99.886	98.808	99.016
	1300-1330	W4-3B	4308	446	1400	98.510	99.565	99.115
	1330-1410	W4-3C	ND	540	1117	99.986[b]	99.474	99.294
	Average	W4-3	1559	736	1358	99.461	99.283	99.142
1/14/82	1030-1100	W4-4A	ND	50	312	99.986[b]	99.904	99.612
	1100-1130	W4-4B	33	359	444	99.978	99.312	99.448
	1130-1200	W4-4C	ND	114	144	99.986[b]	99.781	99.821
	1200-1230	W4-4D	21	684	225	99.986	98.689	99.720
	1300-1330	W4-4E	ND	1466	146	99.986[b]	97.190	99.818
	Average	W4-4	23	535	254	99.984	98.975	99.684

(continued)

TABLE 5-4 (continued)

Date	Bag collection time	Run number	Corrected stack gas concentration[a], ppb			Destruction and removal efficiency, %		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
1/26/82	1340-1410	W4-5A	3136	ND	447	98.910	99.961[c]	99.716
	1415-1445	W4-5B	693	62	2484	99.759	99.939	98.422
	Average	W4-5	1915	51	1466	99.335	99.950	99.069
1/28/82	1200-1230	W6-1A	611	423	250	99.315	-[e]	-[e]
	1315-1400	W6-1B	1268	151	1448	98.579	-[e]	-[e]
	1415-1515	W6-1C	574	129	391	99.357	-[e]	-[e]
	1530-1605	W6-1D	473	198	350	99.470	-[e]	-[e]
	1625-1700	W6-1E	540	243	327	99.396	-[e]	-[e]
	Average	W6-1	693	229	330	99.223	-[e]	-[e]
2/07/82	1100-1145	W5-1A	2097	793	666	91.475	98.738	99.390
	1145-1230	W5-1B	2996	270	723	87.821	99.570	99.337
	1230-1315	W5-1C	355	348	497	98.557	99.446	99.544
	1400-1500	W5-1D	3215	1668	501	86.930	97.345	99.541
	1500-1535	W5-1E	1898	2094	487	92.284	96.667	99.554
	1550-1620	W5-1F	639	1690	340	97.402	97.310	99.688
	1625-1650	W5-1G	350	443	200	98.577	99.295	99.817
	Average	W5-1	1650	1044	488	93.292	98.388	99.553
2/08/82	1145-1245	W5-2A	976	1658	787	96.822	97.886	99.422
	1245-1345	W5-2B	1375	3675	1304	95.523	95.313	99.042
	1345-1430	W5-2C	1182	4033	514	96.152	94.857	99.623
	1430-1500	W5-2D	1219	4195	308	96.031	94.650	99.774
	1515-1600	W5-2E	372	1735	766	98.789	97.787	99.437

(continued)

TABLE 5-4 (continued)

Date	Bag collection time	Run number	Corrected stack gas concentration[a], ppb			Destruction and removal efficiency, %		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
2/09/82	1400-1440	W4/6-1A	209	118	1017	99.874	99.484	96.921
	1445-1530	W4/6-1B	899	1710	3957	99.459	92.528	88.019
	1715-1805	W4/6-1C	458	1830	2069	99.724	92.003	93.735
	1945-2015	W4/6-1D	29	354	714	99.983	98.453	97.838
	Average	W4/6-1	399	1003	1939	99.760	95.617	94.129
2/10/82	0815-0840	W4/6-2A	221	54	406	99.913	99.846	99.198
	0840-0910	W4/6-2B	1575	4137	216	99.382	88.209	99.573
	0910-1000	W4/6-2C	216	2533	454	99.915	92.781	99.103
	1000-1100	W4/6-2D	1366	4264	294	99.464	87.847	99.419
	Average	W4/6-2	845	2747	346	99.668	92.171	99.325
2/10/82	1125-1205	W4/6-3	266	109	666	99.564	98.703	94.512
2/12/82	0730-0755	W4/6-4A	1054	15	1227	99.047	99.901	94.419
	0800-0820	W4/6-4B	1613	ND	1198	98.541	99.937[c]	94.550
	0830-0850	W4/6-4C	732	ND	2051	99.338	99.937[c]	90.670
	0900-0920	W4/6-4D	371	16	1697	99.665	99.892	92.281
	0945-1000	W4/6-4E	484	31	1408	99.562	99.797	93.595
	1015-1030	W4/6-4F	1615	19	1811	98.540	99.875	91.762
	1040-1050	W4/6-4G	841	23	2526	99.240	99.849	88.510
	Average	W4/6-4	959	15	1703	99.133	99.901	92.253

(continued)

TABLE 5-4 (continued)

Date	Bag collection time	Run number	Corrected stack gas concentration[a], ppb			Destruction and removal efficiency, %		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
2/12/82	1600-1700	W4/6-5A	1188	95	443	99.563	99.746	99.180
	1700-1730	W4/6-5B	1684	213	3064	99.380	99.431	94.657
	1730-1820	W4/6-5C	1659	1721	3011	99.389	95.401	94.425
	1830-1915	W4/6-5D	1408	1281	3801	99.482	96.577	92.962
	1920-1935	W4/6-5E	1213	1341	825	99.554	96.416	98.467
	Average	W4/6-5	1430	930	2229	99.474	97.515	95.873

[a] Reported ppb values have been corrected by subtracting average background levels in stack gas.

[b] Calculated using detection limit of 20 ppb.

[c] Calculated using detection limit of 40 ppb.

[d] Calculated using detection limit of 0.8 ppb.

[e] Not present in waste fuel.

As discussed in Section 2.3.5, the waste fuel injection had to match the fuel oil injection pattern in order to prevent flame impingement on the inner wall of the kiln and pre-ignition, or back-puffing, of the fuel oil stream. Appendix B contains a recommended method to utilize waste fuel atomization within the constraints of kiln flame shape.

The ease of incinerability and the completeness of destruction of chlorinated hydrocarbons and other organic compounds depend strongly on the molecular structure of the specific chlorinated compound. Highly chlorinated, low molecular weight hydrocarbons such as carbon tetrachloride, chloroform, and methylene chloride, are characterized by low heats of combustion, high activation energies, and low frequency factors for thermal oxidation reactions. Rather than being considered as fuels, these compounds are often used for inhibition of the combustion of fuels because of their ability to remove hydrogen atoms from the free-radical branching combustion reactions to form HCl.

As the length of the aliphatic hydrocarbon chain is increased, with a comcomitant reduction in the chlorine to carbon ratio, the heat of combustion increases and the kinetic parameters for thermal oxidation (lower activation energies, higher frequency factors) promote a much higher destruction efficiency by incineration. This effect of the chlorine content of the hydrocarbon in influencing destruction efficiency by thermal means would be expected to hold true for aliphatic, aromatic or condensed aromatic structures.

The kinetic mechanism of thermal oxidation of low molecular weight, highly chlorinated hydrocarbons may very well begin with a thermal degradation reaction where HCl is eliminated from the molecule followed by oxidative reactions of the remaining hydrocarbon structure. The mechanism of thermal oxidation of higher molecular weight halocarbons would probably be similar in that cleavage of a -C-C- bond would occur at a early time, before oxidative reactions began. This later mechanism would require a much lower activation energy and result in a more efficient destruction of the molecule at lower temperatures and lower overall residence times in the incineration process.

5.2 PRODUCTS OF INCOMPLETE COMBUSTION (PIC's)

Other compounds were detected by the GC/EC during the analyses for the POHC's, which eluted at retention times of 0.51 min (CH_2Cl_2), 0.80 min ($CHCl_3$), and 1.01 min (CCl_4). The most commonly seen compound had a retention time of 0.57 to 0.61 min, which a post-test laboratory experiment with duplicate GC conditions tentatively identified as trichlorotrifluoroethane. This compound most probably was Freon 113 from the lab trailer air conditioner. Another compound which was seen in several instances eluted at about 1.1 min and was tentatively identified as trichloroethylene, a likely

PIC from combustion of chloromethanes. 1,1,1-trichloroethane (1.54 min R.T.), tetrachloroethylene (1.68 min R.T.), acetone (2.11 min R.T.), acetonitrite (2.15 min R.T.), and acrylonitrile (2.16 min R.T.) were never detected by the in-field GC/EC analyses.

The SASS samples collected for chlorinated dioxins and chlorinated dibenzofurans were also analyzed for products of incomplete combustion. Four samples (one baseline and 3 waste burning) were analyzed for PIC's. The baseline sample was analyzed since the cement plant burns fuel oil as its primary energy source. During the program, fuel oil accounted for 87 to 100% of kiln's energy requirement. Products of incomplete fuel oil combustion need to be distinguishable from products of incomplete hazardous waste combustion - hence the baseline sample. Three SASS samples were collected during hazardous waste burning representing different feed compositions, feed rates and operating conditions. Specific tests results are shown in Table 5-5, which contains positive and tentative identification as well as mass emission rates.

The PIC's which were not detected during the baseline test and can be considered attributable to hazardous waste burning are:

- Benzaldehyde (9.8-17.8 mg/hr)
- Phenol (2.4-11.0 mg/hr)
- C_3-alkylbenzene (3 mg/hr)
- Ethanone, 1-phenyl (6.1 mg/hr)
- Benzoic acid (3.5-47.5 mg/hr)
- C_2-benzoic acid, methyl ester (6.3 mg/hr)
- C_2-naphthalene isomers (10-50 mg/hr)
- C_3-naphthalene isomers (14-46 mg/hr)
- Sulfur (S_6) (15 mg/hr)
- Anthracene (1.5-4.0 mg/hr)

5.3 CHLORINE MATERIAL BALANCE IN CEMENT KILNS DURING THE USE OF CHLORINATED HAZARDOUS WASTE AS AUXILIARY FUEL

The combustion of chlorinated hazardous wastes as auxiliary fuel in cement kilns results in the generation of hydrogen chloride (HCl) in the kiln. Hydgrogen chloride can be absorbed by the clinker product, cement kiln lining, baghouse dust or emitted as part of the particulate. Unabsorbed HCl will be emitted from the stack as will the unburned chlorinated hydrocarbons. The purpose of this section of the report is to present the results of testing conducted at San Juan Cement as they demonstrate the fate of chlorine in the cement kiln process. This section will address the combustion chemistry, possible HCl absorption mechanisms, and theoretical impact of chlorine fate on fuel savings. Results of tests will be presented as well as the chlorine material balance for the kiln.

TABLE 5-5. MASS EMISSION RATE OF PRODUCTS OF INCOMPLETE COMBUSTION AS DETERMINED BY GC/MS ANALYSIS OF SASS TRAIN SAMPLES, mg/hr

Compound	Retention time, min	Run number			
		BW-SASS	W3-1	W4-4	W6-1
Unknown	3.52	74.06	37.03		
Unknown	4.00				37.57
C_2-alkyl benzene, isomer and/or cyclopentene, 1-ethenyl-3-methylene and/or isomer	4.03				1.98
1,3,5,7-Cyclooctatetraene and/or bicyclo(4,2,0) octa-1,3,5-triene and/or benzene ethenyl- and/or isomers of above	4.52				5.27
Benzaldehyde	6.18		9.84		17.79
C_2-benzene, isomer	6.22	13.11			
Phenol	6.80		10.99		2.44
50% phenol, 50% phenol-d_5	6.82			8.45	
Cyclotetrasiloxane, octamethyl	7.28	1.97			3.30
Mixture of ~75% C_3-alkyl benzene + ~25% benzaldehyde, hydroxy isomer	8.27				4.22
Ethanone, 1-phenyl	8.82				6.13
Cycloprop(a)indene, 1,1a,6,6a-tetrachydro- and/or isomer and/or IH-indene, methyl-isomer	10.53	0.66			

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number			
		BW-SASS	W3-1	W4-4	W6-1
Naphthalene and/or azulene and/or isomer	10.73				9.89
Unknown substituted benzene	10.87	4.59			5.93
Unknown substituted benzene	11.20	3.54	3.12	12.75	6.85
Naphthalene and/or azulene and/or isomer	11.27			32.62	3.95
Unknown substituted benzene	11.30	0.98			
Unknown	11.50			12.16	
Benzoic acid	11.60		3.47	38.55	47.45
Unknown	12.03			6.97	
Ethanone, ethyl phenyl- and/or ethanone dimethyl phenyl isomer	12.95				5.67
C_2-benzoic acid methyl ester	13.60				6.33
Unknown	14.98				5.87
1,1'-biphenyl and/or acenaphthylene, 1,2-dihydro and/or isomer	15.03		38.76	6.38	7.25
C_2-naphthalene isomer	15.23		10.41		
C_{14}-alkane isomer	15.35		23.20		

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number			
		BW-SASS	W3-1	W4-4	W6-1
C_2-naphthalene isomer	15.43		47.44		
C_2-naphthalene isomer	15.68		50.91		
C_2-naphthalene isomer	15.75		30.08		
C_2-naphthalene isomer	16.00		33.09		
C_2-naphthalene isomer	16.27		13.31		
Unknown	16.90	17.11			
Benzene, 1,1'-ethylidene bis- and/or benzene, 1-methyl-4-(phenyl methyl)- and/or 1,1'-biphenyl, 2-ethyl- and/or isomers of above	16.90			41.51	
C_{15}-alkane	16.95		35.00		
Sulfur (S_8)	16.98				15.16
Unknown hydrocarbon	17.0				3.56
Mixture of ~90% C_{15}-alkane + ~10% unknown	17.02		32.40		
C_3-naphthalene isomer	17.08		30.66		
1,2-benzenediol, 4-(1,1-dimethyl ethyl)- and/or isomers	17.23			25.21	

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number BW-SASS	 W3-1	 W4-4	 W6-1
Unknown	17.28				14.50
C_3-naphthalene isomer	17.40		13.88		
C_3-naphthalene isomer	17.43		32.40		
C_3-naphthalene isomer	17.52		34.71		
C_3-naphthalene isomer	17.77		46.28		
C_3-naphthalene isomer	18.02		30.66		
Mixture of ~50% unknown phthalate + ~50% unknown hydrocarbon	18.60	4.13	5.32		6.13
1,1'-biphenyl-diethyl- and/or isomer	19.45			68.20	
1,1'-biphenyl-diethyl- and/or isomer	19.93			83.00	
Alkane, $>C_{12}$	20.00	4.78			
Unknown mixture	20.03		28.93		
Alkane, $>C_{13}$	20.10	6.55	13.88		
Unknown	20.12		46.28		
Anthracene and/or phenanthrene and/or benzene, 1,1'-(1,2-ethendiyl)bis- and/or isomers of above	21.18	7.87			

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number BW-SASS	 W3-1	 W4-4	 W6-1
Unknown mixture ~60% sulfur + ~30% anthracene + ~10% unknown	21.22		4.86	12.45	10.74
C_{18} alkane	21.40	7.87			
Unknown mixture	21.50		52.07		10.54
Alkane, $>C_{14}$	21.53	6.39	15.62		
Ethane, 1,1-bis(p-ethyl phenyl)- and/or cyclopenta-(a)indene, 3,8-dihydro-1,2,3,3,8,8-hexamethyl- and/or benzene, 1,1'-(1,2-ethanediyl)bis(3,4-dimethyl)- and/or isomers of above	21.62			12.75	
Unknown	21.78			11.27	
Ethane, 1,1-bis(p-ethyl phenyl)- and/or cyclopenta-(a)indene, 2,8-dihydro-1,2,3,3,8,8-hexamethyl- and/or benzene, 1,1'-(1,2-ethanediyl)bis(3,4-dimethyl- and/or isomers of above	22.10			8.60	
Unknown mixture	22.17		3.64		
Unknown mixture	22.37			8.15	
Unknown mixture	22.63		4.34		
C_{19}-alkane	22.73	11.80			

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number BW-SASS	W3-1	W4-4	W6-1
Unknown mixture	22.77		12.84		
Mixture of ~70% benzo(c)cinnoline + ~30% phenanthrene methyl (isomer)	22.82	4.65			
Unknown mixture	23.52		1.74		
Unknown mixture	23.55	4.59			
Unknown phthalate	23.67	4.72			5.34
Unknown	23.72	2.75			
Unknown mixture	23.78		5.79		
Unknown mixture	23.95		1.10		
C_{20}-alkane	24.00	9.18			
Unknown	24.50	2.03			
Sulfur (S_8)	24.52	68.82	830.78	2825.39	340.07
Pyrene and/or fluoranthene and/or isomer	24.83	7.21			
Unknown mixture	24.93		8.10		
Alkane, $>C_{15}$	25.22	9.83			
Unknown mixture	25.35		3.07		

(continued)

TABLE 5-5 (continued)

Compound	Retention time, min	Run number			
		BW-SASS	W3-1	W4-4	W6-1
Unknown	26.37	7.21			
Unknown	27.48	7.21			
Unknown phthalate	27.73	7.87		23.72	23.73
Alkane, $>C_{13}$	28.53	7.87			
Unknown	28.85	6.55			
1-phenanthrene-carboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methyl-ethyl)-[1R-(1, alpha,4a,beta,10a,alpha)]- and/or isomer	29.10	6.55			
Chrysene and/or isomer	29.30	1.84			
Alkane, $>C_{13}$	29.58	6.55			
Unknown phthalate	30.15		322.82		
Alkane, $>C_{14}$	30.57	5.64			
Alkane, $>C_{12}$	31.50	5.90			
C_{15}-alkane	32.42	4.92			
C_{15}-alkane	33.32	5.64			
Unknown	34.17	3.34			
Unknown	35.00	3.60			

5.3.1 Combustion Chemistry

Wastes burned at San Juan Cement contained methylene chloride, chloroform, and carbon tetrachloride as shown in Section 3 of this report. A condensed summary of the waste analyses is given in Table 5-6.

TABLE 5-6. CHLORINATED HYDROCARBON CONTENT OF WASTES TESTED

Waste batch no.	Methylene chloride, wt %	Chloroform, wt %	Carbon tetrachloride, wt %	Total chlorine, wt %
1	35.1	1.6	1.4	32.0
2	24.8	1.3	1.1	22.9
3	17.2	5.4	2.4	21.4
4	15.8	7.9	16.1	35.1
5	1.9	6.1	12.7	18.7
6	7.6	0.2	0.02	6.5

Theoretically complete oxidation products of combustion of methylene chloride, chloroform, and carbon tetrachloride are shown below. The combustion reactions for all three compounds show a reversible reaction affecting the balance of hydrogen chloride gas to chlorine gas.

Methylene Chloride Combustion Products:

$$\begin{array}{l} 2CH_2Cl_2 + 3O_2 \rightleftarrows 2CO_2 + 2H_2O + 2Cl_2 \\ 2Cl_2 + 2H_2O \rightleftarrows 4HCl + O_2 \\ \hline 2CH_2Cl_2 + 2O_2 \rightleftarrows 2CO_2 + 4HCl \end{array} \qquad \text{(overall)}$$

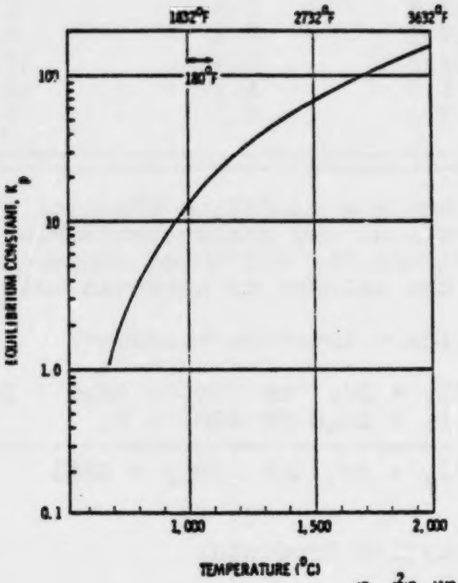
Chloroform Combustion Products:

$$\begin{array}{l} 2CHCl_3 + 2O_2 \rightleftarrows 2CO_2 + 2HCl + 2Cl_2 \\ 2Cl_2 + 2H_2O \rightleftarrows 4HCl + O_2 \\ \hline 2CHCl_3 + O_2 + 2H_2O \rightleftarrows 2CO_2 + 6HCl \end{array} \qquad \text{(overall)}$$

Carbon Tetrachloride Combustion Products:

$$\begin{array}{l} CCl_4 + O_2 \rightleftarrows CO_2 + 2Cl_2 \\ 2Cl_2 + 2H_2O \rightleftarrows 4HCl + O_2 \\ \hline CCl_4 + 4H_2O \rightleftarrows CO_2 + 4HCl \end{array} \qquad \text{(overall)}$$

The conversion of chlorine gas to hydrogen chloride is favored by high temperatures and high water content in the combustion gas. Typically, the burning zone temperature in a cement kiln is 1425°C (2600°F) with the moisture content equal to about 10-15%. Additional moisture is added to the combustion gases in wet process cement kilns in the slurry drying zone of the kiln. Figure 5-2 shows the impact of temperature on the equilibrium constant for the chlorinated compound oxidation reaction. Equilibrium calculations show that 99.987% of the chlorine in the combustion gases will be present as HCl; only 0.013% of the chlorine will be present as chlorine gas.



$$K_p = \frac{(P_{HCl})^2 (P_{O_2})^{1/2}}{(P_{H_2O})(P_{Cl_2})}$$

Figure 5-2. Equilibrium constant versus temperature.

5.3.2 Chlorine Material Balance Tests

The conversion of chlorinated hydrocarbons to HCl was discussed above. Tests at San Juan Cement were conducted to determine the fate of HCl in their cement kiln. Figure 5-3 shows a schematic flow diagram for wet process cement kilns. The chlorine material balance tests were conducted using the following process streams:

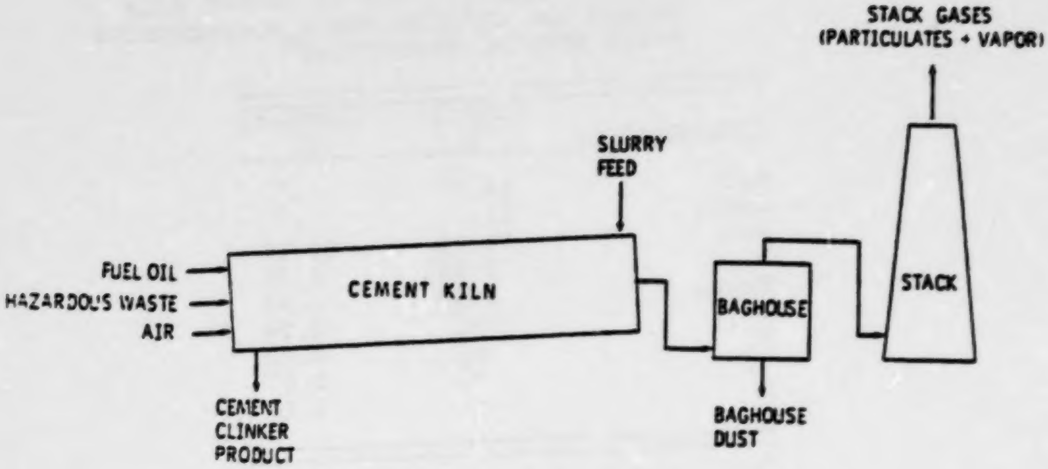

STACK GASES
(PARTICULATES + VAPOR)
SLURRY FEED
FUEL OIL
HAZARDOUS WASTE
AIR
CEMENT KILN
BAGHOUSE
STACK
CEMENT CLINKER PRODUCT
BAGHOUSE DUST

Figure 5-3. Schematic diagram of cement kiln burning hazardous wastes.

Inputs	Outputs
· fuel oil	· clinker product
· hazardous waste	· baghouse dust
· slurry feed	· stack emissions - particulates - HCl vapor - unburned chlorinated hydrocarbons

Table 5-7 shows typical compositions of cement kiln slurry and clinker product when the cement kiln is not burning hazardous waste (baseline tests). The slurry which the kiln was assumed to account for about 11.3 kg/hr (0.056% of dry slurry materials) of chlorine feed to the kiln.

Table 5-8 shows the results of the chlorine material balance tests in the cement kiln. the material balance closure for chlorine ranged from 83.2% to 103.6% with an average closure of 92.3% (100.0% closure is ideal). A comparison of data in Table 5-8 for total chlorine in feed and chlorine in clinker product shows that about 82% of the chlorine fed to the cement kiln will appear in the clinker product. The amount of chlorine in the clinker is presumed to be dependent, primarily, upon quarry alkalinity.

The amount of chlorine appearing in the baghouse dust varies from 5% to 26% of the total chlorine feed. The amount of chlorine appearing in the baghouse dust is influenced by the concentration of chlorine in total fuel (fuel oil plus hazardous waste).

TABLE 5-7. TYPICAL COMPOSITIONS OF CEMENT KILN SLURRY AND CLINKER UNDER NONHAZARDOUS WASTE BURNING CONDITIONS[a]

Component	Slurry, %	Clinker, %
H_2O	36.7[b]	-[c]
$CaCO_3$	80.3	-[c]
SiO_2	14.33	22.18
Al_2O_3	3.80	5.75
Fe_2O_3	1.60	2.52
SO_3	-[c]	0.24
Na	-[c]	0.13
Cl	-[c]	0.07
K	-[c]	0.15

[a] All values on a dry basis except water which is on a wet basis.

[b] Wet basis.

[c] Unknown.

Figure 5-4 shows the dramatic increase in chlorine concentration in baghouse dust when chlorine represents 3% or more of the total fuel. This corresponds to 11.2 lb chlorine per ton of clinker. The plant always went into an upset condition about 90 minutes after the start of a trial burn which had 3% or more of chlorine in the total fuel.

The amount of chlorine appearing in the stack emissions as unburned chlorinated hydrocarbons ranged from 0.076 to 4.3% which represented appropriate overall destruction and removal efficiencies (DRE) of 99.924% down to 95.7% on a total chlorinated hydrocarbons feed basis. The tests showed lower DRE's when burning higher levels of carbon tetrachloride. Compound specific data on DRE's is given in Section 5.1 of this report. The absorption of HCl by the cement kiln process averaged 99.7% in seven tests.

5.3.3 Material Balance Results

The amount of fuel savings that cement kilns can realize by burning chlorinated hazardous waste is dictated by cement product acceptability and by environmental acceptability of stack emissions. The maximum amount of chlorine allowed in the clinker is 0.4-0.5% since chlorine adversely affects cement tensile strength and set time. The amount of chlorine appearing in the clinker will determine the amount of fuel savings which can be realized. As stated above, about 82% of the chlorine in the total fuel appeared in the clinker at San Juan Cement. Other cement plants with different

TABLE 5-8. CEMENT KILN CHLORINE MATERIAL BALANCES (all entries are lb/hr except material balance closure)

	Materials to kiln				Materials from kiln						
Description	Slurry	Fuel oil	Hazardous waste	Total in	Clinker product	Baghouse dust	Stack particulates	Stack HCl	Stack organics	Total out	Material balance closure, %
Total solids + liquids	70,000[a]	12,500	-	82,500	31,100	3,100	20	-	-	34,220	100
Chlorine only shown below											
No waste firing											
BW-SASS	25	0	-	-	21.8	27.9	0.21	NA	0.195	-	-
BW (10/27/81)	25	0	-	-	21.8	12.4	0.095	NA	NA[b]	-	-
BW (10/29/81)	25	0	-	-	21.8	6.2	0.048	NA	NA	-	-
BW (10/14/81)	25	0	-	-	21.8	3.1	0.024	NA	NA	-	-
BW (11/8/81)	25	0	-	-	21.8	3.1	0.024	0.34	NA	25.2	101
Waste firing											
W2-1	25	0	102	127	104	NA	NA	0.65	0.097	105.6	83.2
W2	25	0	462	487	399	NA	NA	0.44[d]	0.72	NA	Indeterminate[c]
W1-2	25	0	462	487	399	104	0.8	0.44[d]	0.50	504.3	103.6
W3-SASS-1	25	0	213	238	195	15.5	0.1	0.64	2.30	213.5	89.7
W3-2	25	0	426	451	369	71.1	0.46	1.58	1.98	444.1	98.5
W3-3	25	0	507	532	435	NA	NA	1.20	3.59	NA	Indeterminate[c]
W4-1	25	0	188	213	174	11.2	0.07	1.14	9.15	195.6	91.8
W4-2	25	0	376	401	328	16.1	0.1	0.55	4.98	349.7	87.2
W4-3	25	0	423	448	367	NA	NA	0.96	6.33	NA	Indeterminate[c]

[a] Contains 25,690 lb H_2O and 10,090 lb CO_2 not shown as leaving kiln.

[b] Not analyzed.

[c] Unable to calculate since 2 or more variables were not analyzed.

[d] Estimated values.

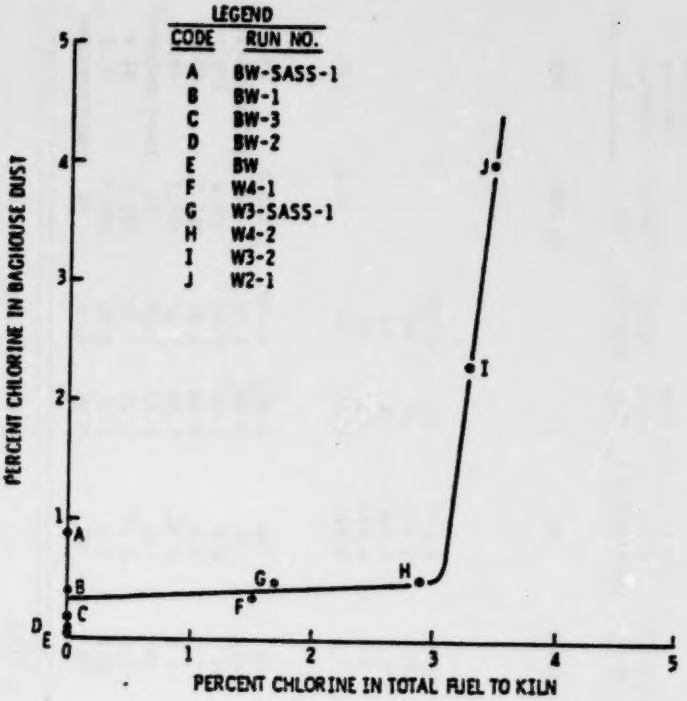


Figure 5-4. Effect of chlorine concentration in total fuel (fuel oil + hazardous waste) on chlorine content of baghouse dust at San Juan Cement.

slurry feed composition and alkalinity will realize different results, e.g., up to 92% of the clorine was retained at St. Lawrence Cement in Mississauga, Ontario during those tests [12].

Chlorine content of total fuel feed has another dramatic impact cement clinker compositions. Figure 5-5 shows changes in sodium and potassium clinker concentrations as a function of the chlorine content of clinker. Clinker has the following approximate specifications in order to be considered saleable:

Chlorine: ≤ 0.5%
Potassium: ≲ 0.9%
Sodium: ≲ 0.2%

Increases over these amounts reduce tensile strength and increase set-time for cement product to the point where its use would endanger public welfare in construction.

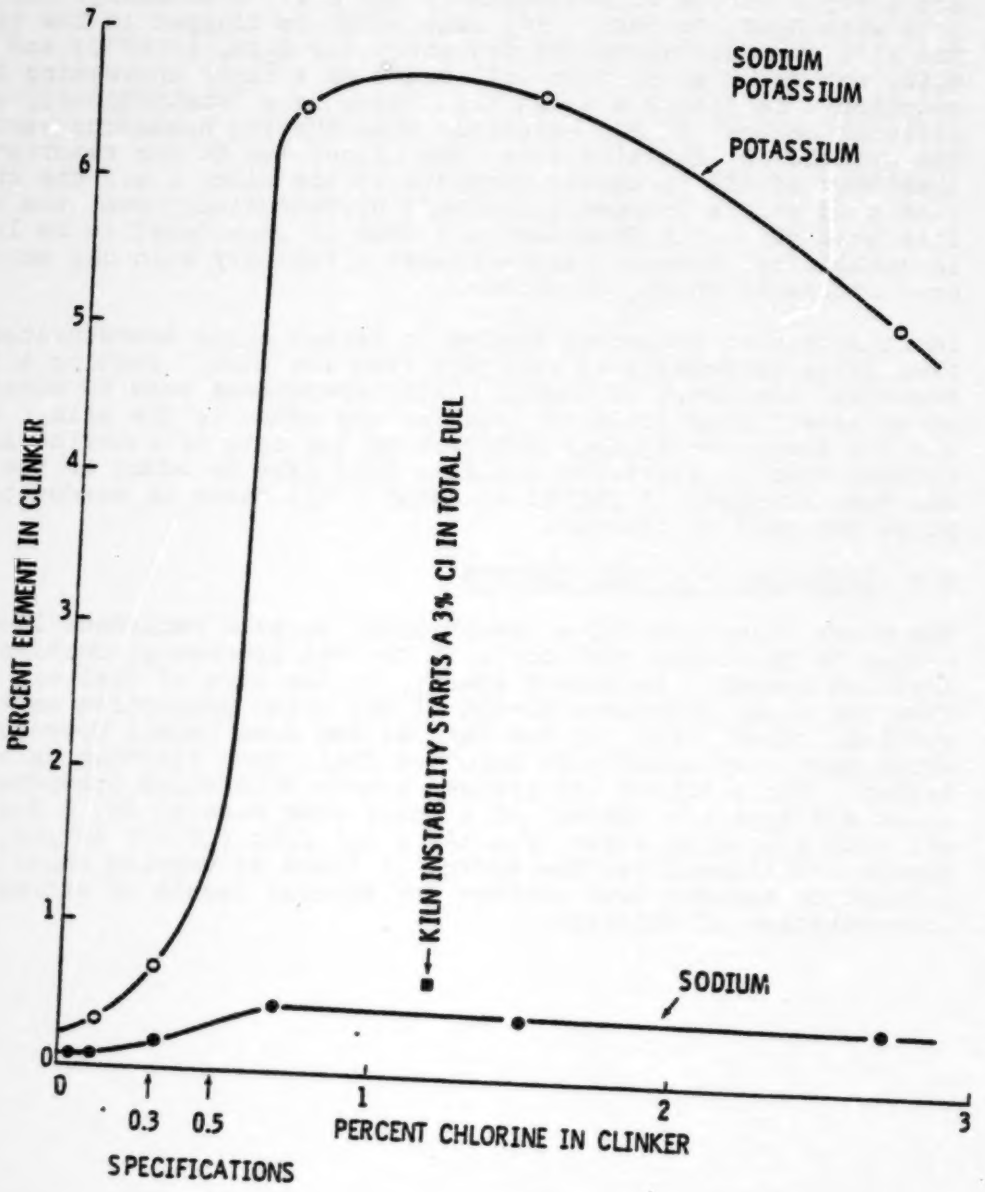


Figure 5-5. Impact of clinker chlorine content on clinker sodium and potassium contents.

Normally, the potassium leaves the kiln as potassium sulfate and potassium oxide and is collected in the baghouse. Cement plants are a major source of potassium in the U.S. Presumably, HCl reacts with K_2SO_4 to form a KCl salt which is trapped in the clinker. The kiln operates above the dew point for H_2SO_4 ($\sim$160°C) and any H_2SO_4 not absorbed by dust will leave as a vapor increasing SO_x emission. Section 4.4 shows that there is a "statistically significant change" in SO_x emissions when burning hazardous waste. The average SO_x emission rates are higher due to the reaction chemistry of the inorganic elements in the kiln; i.e., the chlorine acid gas is trapped (scrubbed) preferentially over the sulfate acid gas. San Juan Cement's feed is considered to be low in alkalinity, however, and a higher alkalinity kiln may not show increases in SO_x emissions.

Incineration of hazardous wastes in cement kilns demonstrated a time delay in release of chlorine from the kiln. Section 4.7 described the onset of unstable kiln operations some 90 minutes after excess quantities of chlorine are added to the kiln. Figure 5-6 shows the dynamic behavior of the fate of chlorine in clinker when an excessive chlorine feed rate is added to the kiln and then stopped. A period of about 3 1/2 hours is needed to purge the kiln of chlorine.

5.4 POTENTIAL FOR FUEL SAVINGS

The major objective for a cement plant to burn hazardous liquid wastes is to offset fuel costs in the wet process production of portland cement. Purchased energy, in the form of fuel oil to fire the kiln, comprises 30-40% of the total production cost of portland cement [33]; in the case of San Juan Cement Company, which must rely totally on imported fuel, that fraction is even higher. For a single wet process rotary kiln which produces about 6.3 kg/s (25 ton/hr) of clinker when burning No. 6 fuel oil with a heating value of 4.184×10^7 J/kg (18,000 Btu/lb), Figure 5-7 illustrates the effect of fuels of varying chlorine content on maximum fuel savings for several levels of clinker incorporation of chlorine.

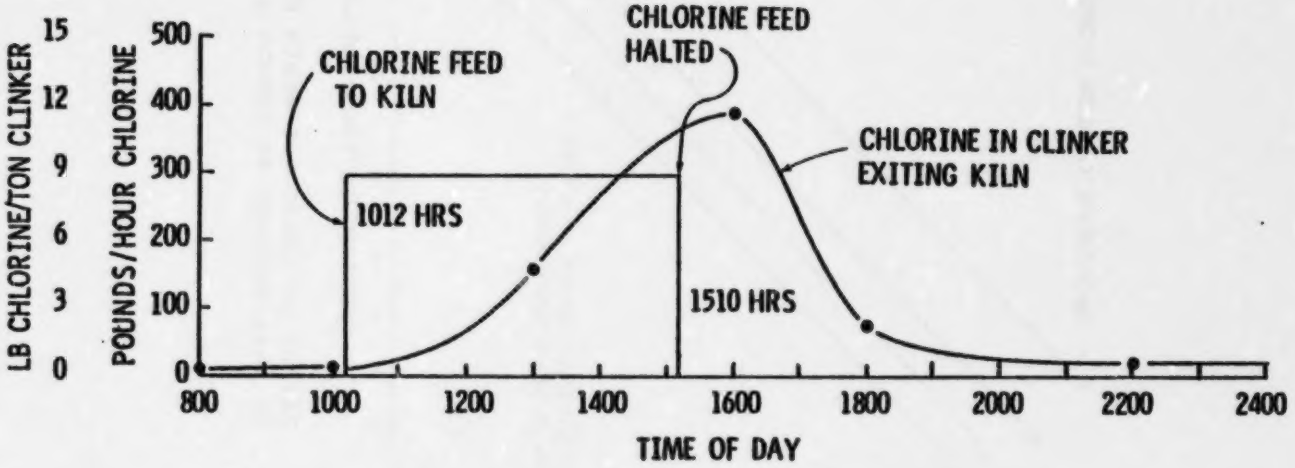


Figure 5-6. Fate of added chlorine in cement clinker production.

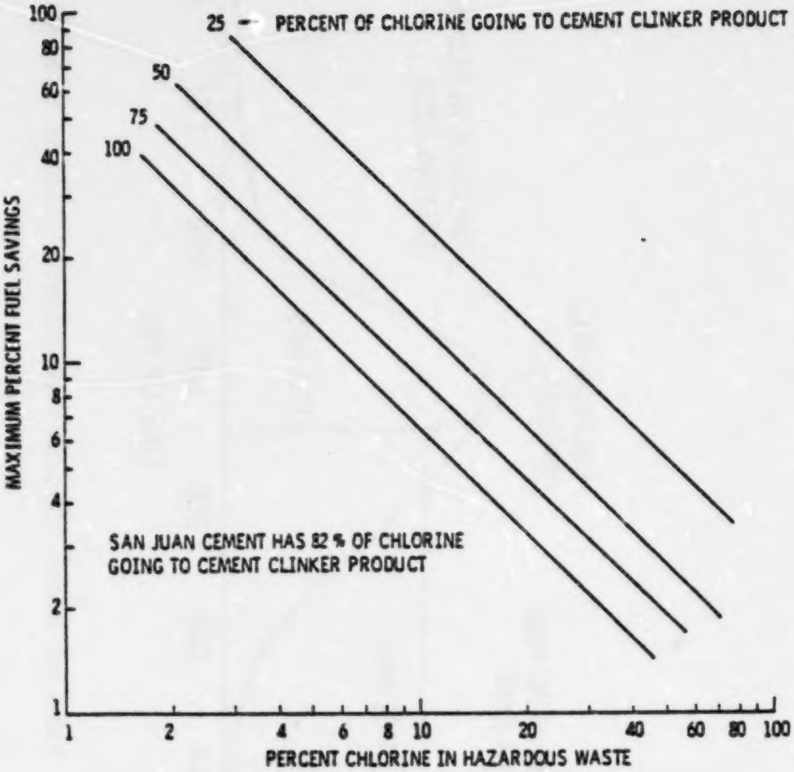


Figure 5-7. Effect of hazardous waste chlorine content on fuel savings at cement plants.

SECTION 6

CONCLUSIONS

The purposes of the demonstration program were to generate permit evaluation criteria for the EPA, to demonstrate that hazardous chlorinated chemical wastes could be safely and effectively used as supplemental fuel in wet process cement kilns during the production of saleable portland cement, and to recommend techniques for the proper management of waste fuel programs at industrial kiln plants. These objectives included determining the destruction and removal efficiencies of the principal organic hazardous constituents in the waste fuel, the products of incomplete combustion, the differences in emission levels of conventional pollutants, the effects on clinker quality and kiln refractory lining integrity, the effects on ambient air quality, the presence or absence of dioxins and dibenzofurans, the effects of transition from normal kiln operation to waste burning, the chlorine material balance, possible monitoring techniques for enforcement purposes, and the magnitude of possible fuel savings. All of these ambitious objectives were met as presented below.

1. Occasional achievement of 99.99% destruction and removal efficiency for methylene chloride and chloroform was demonstrated. Carbon tetrachloride never demonstrated 99.99% destruction and removal efficiency (DRE). The inability to consistently achieve 99.99% DRE is attributed to the absence of waste atomization and the high chlorine content of the species being tested. These three compounds (CH_2Cl_2, $CHCl_3$, and CCl_4) are occasionally employed as fire retardants because of their ability to remove hydrogen atoms from the free-radical branching combustion reactions to form HCl. Chlorinated species containing less chlorine will have different combustion characteristics and could have higher DRE's.

2. Chlorinated dioxins and chlorinated dibenzofurans are not produced at detectable levels when a cement kiln firing chlorinated wastes is operating normally.

3. Cement kilns will absorb over 99% (about 99.7%) of the HCl formed during the combustion of chlorinated hazardous wastes.

4. At San Juan Cement, approximately 82% of the chlorine fed to the cement kiln appears in the clinker. This limits the chlorine content of total fuel to less than 1%. This may vary at different cement plants since quarry alkalinity (ability to absorb chlorine) varies at each cement plant.

5. Achievable fuel savings are a function of the chlorine content of the waste and each plant's ability to absorb chlorine. At San Juan Cement, a hazardous waste containing less than 5% will result in at least a 20% savings in fuel costs. Higher fuel savings may be possible for higher chlorine contents at other plants.

6. Production of saleable cement product is possible when burning chlorinated hazardous wastes provided the plant's chlorine absorbability limit is not exceeded.

7. Atomization of the waste fuel would be desirable, if a flame configuration can be obtained which does not alter the primary fuel flame configuration.

8. High feed line pressure [1,380-2,070 kPa (200-300 psig)] is not required for waste injection to the kiln. This pressure requirement may change depending on the type of atomizing nozzle used.

9. There is no significant change in particulate emissions due to burning chlorinated hazardous wastes. This result was observed on a cement kiln equipped with a fabric filter air pollution control system. A cement kiln with an electrostatic precipitator may not achieve similar results due to a change in dust resistivity.

10. Emissions of sulfur dioxide, total hydrocarbons, and hydrogen chloride increased significantly when waste was burned. A cement kiln with a higher alkalinity feed than San Juan Cement may not have an increase in SO_2 emissions.

11. Emissions of nitrogen oxides decreased significantly when waste was burned.

12. There is no change in particulate ambient air quality due to hazardous waste combustion in cement kilns.

13. The solid waste (baghouse dust) generated by hazardous waste burning and its RCRA extract (leachate) are suitable for landfilling.

14. Continuous carbon monoxide measurement is not a suitable analytical enforcement technique for cement kilns burning hazardous wastes. Normal process variations influence CO concentrations more than waste burning. (This conclusion applies only to cement kilns; there were no data generated during this program for the utility of CO measurements for incinerators.)

SECTION 7

RECOMMENDATIONS FOR FUTURE STUDY

Hazardous waste incineration in existing large industrial kiln facilities is of growing importance because of the increasing volume of chemical wastes that must be safely destroyed. The study reported herein has been the most comprehensive investigation of the suitability of wet process cement kilns to destroy volatile chlorinated organic wastes.

Based on this work we recommend that the following research areas be included in the development of industrial kiln hazardous waste processing programs:

1. The development and testing of a gas temperature measurement system based on best available thermocouple technology for use in industrial kilns should be pursued. Currently, any correlation of burning zone temperature with DRE cannot be developed because the standard type of burning zone temperature measurement is accomplished with optical pyrometers, which can give misleading results. Such a system must be able to measure temperature with defineable accuracy in the 800 - 1,700°C range, be mechanically stable in the extremely hostile kiln environment, possess minimized radiation effects, and be adaptable to a rotary system.

2. The development and validation of a sampling and analytical technique for very low levels (ppb) of volatile organics (b.p. less than 100°C) is needed in order to demonstrate 99.99% DRE plus an additional significant figure. When a POHC is present in the waste feed in low concentrations (less than 1%) and the exhaust gas has a high volumetric flowrate, problems can be encountered in collecting enough gas sample volume to ensure analytical detection. Many volatile organic compounds are not retained on commonly used sorbent materials, i.e., low breakthrough volumes.

3. An analytical enforcement technique, e.g., use of a continuous monitor, is needed to ensure continued waste destruction after the trial burn testing is complete. Hazardous waste incinerators are required to have carbon monoxide continuous monitors which are coupled to the waste feed

cutoff system and activate when a specified ppm level of CO is exceeded. This program demonstrated that CO monitoring is extremely troublesome and unreliable due to the high levels of H_2O (33%) and CO_2 (17%) which act as positive interferences in the NDIR analyzer and must be precleaned from the sample gas. Also, normal cement process fluctuations affected the CO levels more often and in greater magnitude than the addition of waste fuel to the system.

4. A program should be developed whereby activation energies for ignition of various chlorinated hydrocarbons are measured as a function of molecular structure and chlorine to carbon ratio. Statistical analyses of the data of the data from a predictive model of incineration time-temperature requirements have indicated that autoignition temperature is the most important predictor of compound destructability [34]. A very rapid method of obtaining these data is to use a shock tube as an ignition source or a continuous plug-flow reactor and to measure ignition delays as a function of pressure, temperature, and composition. A plot of the natural log of reciprocal ignition delay versus reciprocal absolute temperature will then give the activation energies for ignition. This experimental method has been commonly used to study the kinetic parameters of oxidation reactions of fuels.

5. The effects on ambient air quality for POHC levels should be investigated, preferably beyond the plant's fencelines. Both passive dosimeters and sorbent resin ambient samplers can operate in the ppb and sub-ppb concentrations which are expected as ambient levels.

SECTION 8

QA/QC RESULTS

The objective of a Quality Assurance/Quality Control program is to assure the precision and accuracy of all data generated. This section presents QA data obtained during the sampling and analytical program. The quality of the QA data illustrate the quality of data presented in the report (Sections 4 and 5) and the significance of conclusions (Section 6).

8.1 WASTE ANALYSIS

All waste fuel samples were collected in amber glass containers, sealed, labeled, and shipped as a hazardous chemical according to DOT regulations. During analysis, method of identification of each component in the waste was by mass spectra (MS) alone or both mass spectra and retention time (MS,RT). Each detected component was quantified relative to a standard volume of that component injected into the GC/MS (external standards of the major components) or another compound which eluted in the vicinity of that compound (minor components). Table 8-1 illustrates the type of waste fuel analysis report which resulted, including the sample log numbers. The waste samples were analyzed in duplicate[a], triplicate, or, in the case of Waste Batch 3, sextriplicate. Waste Batches 4, 5, and 6 were not run in replicate because satisfactory precision on previous samples had been established. Table 8-2 presents the waste fuel GC/MS analysis precision results.

Waste fuel samples from Batches 1, 2, and 3 were also re-analyzed at different times to check on the effect of sample storage time. A waste sample named Waste #3, which was the pre-test sample of Waste Batch 1, was analyzed twice as were Waste #5 (Waste batch 3 pre-test sample) and Waste batch 3 from the test runs. Table 8-3 presents results of these reanalyses. The precision values obtained from comparing these reanalyses compare well with Table 8-2 for the POHC's.

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[a] In the case of only two observations (duplicates) the range is directly related to the standard deviation, i.e., $R = \sqrt{2}\ s$, thus the percent difference is $\sqrt{2}$ times the relative standard deviation or coefficient of variation.

TABLE 8-1. EXAMPLE OF WASTE FUEL ANALYSIS REPORT BY $(GC)^2/MS$

No.	Compound	Retention time, min.	Method of identification	Mass/compound used for quantification	Waste batch #3 1-81-12-03-03[a] 12-9-81	Waste batch #5 1-81-11-20-09[b] 12-9-81
1	Water	0.6	MS, RT	18/Water	4.3	5.9
2	Methanol	0.6	MS, RT	31/Methanol	13.9	7.5
3	Ethanol	0.7	MS, RT	31/Ethanol	8.6	2.8
4	Acetone	0.8	MS, RT	43/Acetone	11.2	12.4
5	Acrylonitrile	0.8	MS, RT	40/Acrylonitrile	1.1	1.5
6	2-Propanol	0.8	MS, RT	45/2-Propanol	5.3	4.7
7	Methylene chloride	0.9	MS, RT	84/Methylene chloride	12.0(13.1)[c]	15.0(21.6)
8	Methyl acetate	0.9	MS, RT	43/Methyl acetate	0.4	0.8
9	C_6-isomer (Unknown #1)	1.0	MS	TI/3-Methyl pentane	1.8	3.4
10	3-Methyl pentane	1.0	MS, RT	TI/3-Methyl pentane	2.7	4.8
11	n-Hexane	1.1	MS, RT	TI/n-Hexane	7.2	12.4
12	Methyl ethyl ketone	1.1	MS, RT	TI or 72/Methyl ethyl ketone	0.08	0.3
13	Chloroform	1.2	MS, RT	83/Chloroform	3.4(2.6)	0.7(0.67)
14	Ethyl acetate	1.2	MS, RT	43/Ethyl acetate	9.0	14.0
15	Unknown #2	1.3	-	TI/Toluene	0.4	0.7
16	Unknown #3	1.4	-	TI/Toluene	0.03	0.1
17	Carbon tetrachloride	1.6	MS, RT	117/Carbon tetrachloride	1.4(1.2)	0.5(0.39)
18	Benzene	1.6	MS, RT	78/Benzene	0.2	0.4
19	Hexamethylsiloxane	1.8	MS	NA	NA	NA
20	Toluene	3.6	MS, RT	TI/Toluene	0.02	0.07
21	Unknown #4	5.5	-	TI/Butyl benzene	0.03	0.09
22	C_5-benzene isomer	15.2	-	TI/Butyl benzene	1.33	0.6
23	Sec-butyl ethyl benzene	16.4	-	TI/Butyl benzene	1.23	1.8
24	Unknown #7 (MW = 202)	22.8	-	TI/Butyl benzene	0.22	0.1

(continued)

TABLE 8-1 (continued)

No.	Compound	Retention time, min.	Method of identification	Mass/compound used for quantification	Waste batch #3 1-81-12-03-03 12-9-81	Waste batch #5 1-81-11-20-09 12-9-81
25	Xylene isomer	6.3	MS	TI/Butyl benzene	0.04	ND
26	Xylene isomer	6.6	MS	TI/Butyl benzene	0.2	ND
27	Dimethyl phenol isomer	10.5	MS	TI/Butyl benzene	0.04	ND
28	Unknown #8	11.1	MS	TI/Butyl benzene	0.13	ND
29	Unknown #9 (MW = 116)	12.5	MS	TI/Butyl benzene	0.05	ND
30	Unknown #10	13.2	MS	TI/Butyl benzene	0.62	ND
31	C_5-benzene isomer	14.4	MS	TI/Butyl benzene	0.08	ND
32	Unknown #11 (MW = 281)	14.9	MS	TI/Butyl benzene	0.22	ND
33	Unknown #12 (MW = 182)	15.5	MS	TI/Butyl benzene	0.72	ND
34	Unknown #13 (MW = 180)	17.2	MS	TI/Butyl benzene	0.17	ND
35	Unknown #14 (MW = 264)	22.7	MS	TI/Butyl benzene	0.77	ND
36	Unknown #15	25.5	MS	TI/Butyl benzene	0.28	ND
37	Unknown #16 (MW = 346)	26.6	MS	TI/Butyl benzene	0.22	ND
38	1,1'-(1,2-ethanedyl)bis(4-methoxy benzene)	27.0	MS	TI/Butyl benzene	0.23	ND
					89.6	90.6

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[a] MRC sample identification number.

[b] MRC sample identification number.

[c] Values in parentheses were determined with GC/EC.

TABLE 8-2. GC/MS ANALYSIS PRECISION RESULTS, RELATIVE STANDARD DEVIATION (%)

Major components	Waste batch #1 log # 1-81-10-09-03	W1-1 log # 1-81-11-02-02	W2-1 log # 1-81-11-18-02	W3 log # 1-81-11-20-09
Water	-[a]	-[a]	-[a]	0
Methanol	11	5	10	13
Ethanol	0	9	25	14
Acetone	8	3	4	4
2-Propanol	9	3	7	10
Methylene chloride	7	4	1	4
C_6-isomer	0	2	0	14
3-Methylpentane	9	1	9	9
n-Hexane	8	8	5	2
Chloroform	10	15	14	9
Ethyl acetate	2	4	12	1
Carbon tetrachloride	8	9	9	0
Toluene	0	0	0	-[a]

[a] Present in trace amount in waste; not a major component.

TABLE 8-3. WASTE FUEL REANALYSIS RESULTS (VOL %)

Major components	Waste sample #3 log # 1-81-10-09-03 Analysis date 10/14/82	 11/03/81	Waste sample #5 log # 1-81-11-20-09 Analysis date 11/23/81	 12/09/81	Waste batch #3 log # 1-81-12-03-02 Analysis date 12/09/81	 1/14/82
Water	-[a]	-[a]	7.5	7.5	4.3	6.4
Methanol	10.4	1.5[b]	4.9	5.9	13.9	14.2
Ethanol	0.8	0.8	3.4	2.8	8.6	9.6
Acetone	14.2	12.4	13.1	12.4	11.2	10.7
Isopropanol	4.7	4.9	5.4	4.7	5.3	6.4
Methylene chloride	24.4	25.2	14.2 (18.4)[c]	15.0 (21.6)[c]	12.0	12.6
Hexane isomer	3.9	3.0	2.8	3.4	1.8	1.5
3-Methylpentane	5.4	4.8	4.2	4.8	2.7	1.8
n-Hexane	19.8	17.6	16.6	12.5	7.2	6.0
Chloroform	1.0	0.8	0.8 (0.6)[c]	0.7 (0.67)[c]	3.4	2.7
Ethyl acetate	4.0	8.3	13.2	14.0	9.0	4.2
Carbon tetrachloride	0.8	0.6	0.5 (0.3)[c]	0.5 (0.39)[c]	1.4	1.3
Toluene	0.2	0.1	NA[d]	0.1	0.02	NA

[a] Trace amount present.

[b] This value is considerably lower because a low level standard was used to quantify during the first analysis and the MS response to methanol was nonlinear. A high level standard was used for the second analysis which was much closer in concentration to the actual sample.

[c] Values in parenthesis are GC/EC confirmation values.

[d] NA = not analyzed.

8.2 POHC ANALYSIS

A description of the sample collection system and procedures for the volatile organic POHC's was given in Section 3.4. The dynamic gas external standards generation system was also discussed in Section 3.4.1.4. The gas chromatograph with electron capture detector was checked each sampling day for response factors of the three chlorinated hydrocarbons chosen as POHC's. From this tabulation kept in the field analyst's laboratory notebook, X-bar control charts were generated which describe the accuracy of analysis based on the reference standards used. Table 8-4 contains the measured response factors (amount in ppb/area) of the GC/EC.

The one excursion off scale for each of the control charts was the incident when the tritium source failed, and was subsequently refoiled.

TABLE 8-4. GC/EC RESPONSE FACTOR TABULATION FOR EACH POHC

Event	Date	Response factor, amount (ppb)/area counts CH_2Cl_2	$CHCl_3$	CCl_4
1	11/15/81	3.5140^{-4}	1.0974^{-4}	9.0739^{-4}
2	11/16/am	8.9407^{-4}	5.8378^{-4}	6.8802^{-4}
3	11/16/pm	8.2007^{-4}	5.3091^{-4}	5.6319^{-4}
4	11/16/pm	7.6358^{-4}	4.8682^{-4}	5.1635^{-4}
5	11/17/am	7.3683^{-4}	4.1748^{-4}	4.3082^{-4}
6	11/18/am	6.8666^{-4}	3.9435^{-4}	4.3082^{-4}
7	11/19/am	6.4931^{-4}	3.7826^{-4}	4.1756^{-4}
8	12/01/am	5.1919^{-4}	3.1007^{-4}	3.5147^{-4}
9	12/01/am	5.0194^{-4}	2.9918^{-4}	3.3852^{-4}
10	12/04/am	4.4774^{-4}	2.6708^{-4}	3.0185^{-4}
11	12/07/am	4.2953^{-4}	2.5622^{-4}	2.8957^{-4}
12	12/08/81	4.1222^{-4}	2.4589^{-4}	2.7790^{-4}
13	1/12/82	1.5953^{-4}	2.8335^{-4}	2.6581^{-4}
14	1/13/82	1.6996^{-4}	2.8596^{-4}	2.8532^{-4}
15	1/28/82	1.7351	2.1821	2.0522
16	2/8/82	7.1396^{-5}	1.1934^{-4}	1.4112^{-4}
17	2/9/82	7.5665^{-5}	1.0506^{-4}	1.4112^{-4}
18	2/11/82	8.1050^{-5}	7.0046^{-5}	5.8072^{-4}
19	2/11/82	8.0066^{-5}	7.4418^{-5}	6.1227^{-4}
20	2/12/82	8.5657^{-5}	8.3958^{-5}	7.6380^{-5}

Each gas sample bag had replicate GC/EC injections made. Blank samples were run after the bag had been purged 4-5X with nitrogen. Blanks were allowed to sit about the same time period as bag samples, from 15-60 minutes. Table 8-5 presents the blank and replicate precision QA/QC results for POHC analyses.

TABLE 8-5. COMPILATION OF REPLICATE PRECISION AND BLANKS FOR ALL POHC's

Date	Bag collection time	Run number	Replicate precision, relative standard deviation (%) CH_2Cl_2	Replicate precision, relative standard deviation (%) $CHCl_3$	Replicate precision, relative standard deviation (%) CCl_4	Blank concentration, ppb CH_2Cl_2	Blank concentration, ppb $CHCl_3$	Blank concentration, ppb CCl_4
11/11/81		BW						
	1100 - 1130	BW-A1	66	-[a]	31	ND[b]	ND	ND
	1300 - 1400	BW-B1	26	0.8	0.4			
	1400 - 1500	BW-C1	-[a]	16	87			
11/12/81		BW						
	1205 - 1300	BW-A2			25	ND	ND	ND
11/18/81		BW						
	1230 - 1330	BW-A3	-	-	37	ND	ND	ND
	1350 - 1445	BW-B3	54	-	19			
	1515 - 1650	BW-C3	-	-	-			
11/16/81		W1-2						
	1050 - 1130	W1-2A	-	-	-	ND	ND	ND
	1205 - 1210	W1-2B	-	-	33			
	1305 - 1410	W1-2C	-	-	47			
	1425 - 1500	W1-2D	-	-	64			
	1525 - 1610	W1-2E	-	-	-			
11/10/81		W2-1						
	1400 - 1430	W2-1	42	-	-	ND	ND	ND
12/03/81		W3-1						
	1000 - 1130	W3-1A	-	-	12	ND	ND	ND
	1130 - 1240	W3-1B	-	74	2			
	1300 - 1530	W3-1C	-	-	-			

(continued)

TABLE 8-5 (continued)

Date	Bag collection time	Run number	Replicate precision, relative standard deviation (%)			Blank concentration, ppb		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
12/04/81		W3-2				ND	ND	ND
	0900 - 0930	W3-2A	11	-	10			
	0940 - 1045	W3-2B	17	141	7			
12/04/81		W3-3				ND	ND	ND
	1415-1530	W3-3A	1	-	51			
	1540-1640	W3-3B	5	-	26			
12/08/81		W4-1				ND	ND	ND
	1420 - 1440	W4-1A	4	15	5			
	1445 - 1500	W4-1B	3	13	2			
	1505 - 1540	W4-1C	3	5	5			
	1545 - 1555	W4-1D	2	1	10			
	1600 - 1624	W4-1E	7	3	1			
12/09/81		W4-2				ND	ND	ND
	0912 - 0935	W4-2A	42	68	42			
	0935 - 1015	W4-2B	3	18	16			
	1030 - 1115	W4-2C	69	49	9			
	1145 - 1220	W4-2D	13	57	17			
	1230 - 1350	W4-2E	5	-	4			
	1415 - 1440	W4-2F	2	-	3			
	1450 - 1515	W4-2G	-	-	24			
12/10/81		W4-3				ND	ND	ND
	1230 - 1300	W4-3A	38	3	23			
	1300 - 1330	W4-3B	4	30	17			
	1330 - 1410	W4-3C	-	41	56			

(continued)

TABLE 8-5 (continued)

Date	Bag collection time	Run number	Replicate precision, relative standard deviation (%)			Blank concentration, ppb		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
1/14/82		W4-4				ND	ND	ND
	1030 - 1100	W4-4A	-	11	6			
	1100 - 1130	W4-4B	4	20	10			
	1130 - 1200	W4-4C	-	25	5			
	1200 - 1230	W4-4D	19	26	2			
	1300 - 1330	W4-4E	-	12	6			
1/26/82		W4-5				ND	ND	ND
	1340 - 1410	W4-5A	20	-	6			
	1415 - 1445	W4-5B	32	14	17			
1/28/82		W6-1				ND	ND	ND
	1200 - 1230	W6-1A	3	16	36			
	1315 - 1400	W6-1B	7	10	15			
	1415 - 1515	W6-1C	49	37	16			
	1530 - 1605	W6-1D	31	23	12			
	1625 - 1700	W6-1E	6	12	10			
2/07/82		W5-1				ND	ND	ND
	1100 - 1145	W5-1A	13	1	5			
	1145 - 1230	W5-1B	10	22	4			
	1230 - 1315	W5-1C	12	13	11			
	1400 - 1500	W5-1D	5	27	13			
	1500 - 1535	W5-1E	17	32	16			
	1550 - 1620	W5-1F	13	27	7			
	1625 - 1650	W5-1G	36	19	11			

(continued)

TABLE 8-5 (continued)

Date	Bag collection time	Run number	Replicate precision, relative standard deviation (%)			Blank concentration, ppb		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
2/08/82		W5-2				ND	ND	ND
	1145 - 1245	W5-2A	31	36	13			
	1245 - 1345	W5-2B	10	22	11			
	1345 - 1430	W5-2C	11	27	6			
	1430 - 1500	W5-2D	6	13	11			
	1515 - 1600	W5-2E	12	37	24			
2/09/82		W4/6-1				ND	ND	ND
	1400 - 1440	W4/6-1A	7	12	5			
	1445 - 1530	W4/6-1B	36	13	15			
	1715 - 1805	W4/6-1C	14	27	14			
	1945 - 2015	W4/6-1D	13	37	37			
2/10/82		W4/6-2				ND	ND	ND
	0815 - 0840	W4/6-2A	23	19	11			
	0840 - 0910	W4/6-2B	2	8	4			
	0910 - 1000	W4/6-2C	14	10	8			
	1000 - 1100	W4/6-2D	4	3	15			
2/10/82		W4/6-3				NA[c]	NA	NA
	1125 - 1205	W4/6-3A	4	54	55			
2/12/82		W4/6-4				ND	ND	ND
	0730 - 0755	W4/6-4A	15	31	11			
	0800 - 0820	W4/6-4B	2	-[a]	5			
	0830 - 0850	W4/6-4C	10	-[a]	13			
	0900 - 0920	W4/6-4D	23	11	8			
	0945 - 1000	W4/6-4E	25	3	3			
	1015 - 1030	W4/6-4F	6	5	5			
	1040 - 1050	W4/6-4G	4	10	1			

(continued)

TABLE 8-5 (continued)

Date	Bag collection time	Run number	Replicate precision, relative standard deviation (%)			Blank concentration, ppb		
			CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
2/12/82		W4/6-5				NA	NA	NA
	1600 - 1700	W4/6-5A	7	22	4			
	1700 - 1730	W4/6-5B	12	15	4			
	1730 - 1820	W4/6-5C	9	33	14			
	1830 - 1915	W4/6-5D	37	28	41			
	1920 - 1935	W4/6-5E	44	21	28			

[a] No precision because compound was below detection limit.

[b] ND = not detected.

[c] NA = no blanks for this run; same day as another run.

8.3 EXHAUST GAS AND METALS ANALYSES

Wherever possible, validated EPA Reference Methods were used to sample and analyze the kiln exhaust gas. Analysis splits and reference standards were run for SO_2, NO_x, and HCl analyses. Because all HCl analyses were run in one batch only one entry is provided. Table 8-6 presents these QA/QC results.

Calibration of the dry gas meters, temperature sensors, analytical balances, orifice and rotameters used for ambient particulate sampling, and analytical reagents was also done for this program. These data sheets are not presented in this report, but are available for review at MRC. These QA/QC activities apply to particulate emissions (EPA Method 5), dry gas analysis (EPA Method 3), volumetric flow rate (EPA Method 2), and SASS train samples. Certified smoke readers conducted the visible emission evaluations.

Table 8-7 contains the QA/QC results of the ICP metals analyses. QA/QC results for the dioxin and dibenzofuran results were shown in Tables 4-13 through 4-20.

TABLE 8-6. QA/QC RESULTS FOR EXHAUST GAS SAMPLE ANALYSIS

Parameter	MRC log number	Splits, mg/dscm Results	Splits, mg/dscm Average	Splits, mg/dscm Relative percent	Standards, mg/dscm Observed value	Standards, mg/dscm True value	Standards, mg/dscm Percent recovery
NO_x	1-81-11-18-02	681.02 623.67	652.35	8.79	652.35	627.45	103:97
	1-81-11-02-02	633.79 608.18	620.99	4.1	620.99	627.45	98.97
	1-81-10-26-03				506.65	428.26	118
	1-81-10-20-04	313.6 245.4	279.5	24.4	279.5	258.95	107.9
	1-82-02-02-01	138.02 111.73	124.88	21	124.9	109.55	114
	1-81-11-20-09	285.71 267.15	276.43	6.7	276.43	258.95	106.8
	1-81-12-08-04	980.4 949.4	964.9	1.6	965	856.5	112.7
	1-81-12-14-03	729.3 858	793.7	8.1	793.65	856.51	92.7
SO_2 Method 6	1-81-11-02-02				235.32 1,866.34	228.78 1,868.4	102.9 99.9
	1-81-10-26-03				233.01	228.78	101.8
SO_2 Method 8	1-81-12-08-04				4,612	4,528	102
	1-81-11-20-09	1,915.7 1,921.8	1,918.7	0.32	1,918.7	1,907.0	100.6
HCl	1-82-02-17-05	291.3 289.0	290.1	0.79	290.1	277	104.7

TABLE 8-7. QA/QC RESULTS OF METAL ANALYSES

Parameter	Record number	Splits, µg/mL			Standards, µg/mL			Spikes, µg/mL			
		Results	Average	Relative percent	Observed value	True value	Percent recovery	Original value	Spike	Original + spike	Percent recovery
Ag	1-81-10-09-03	0.089 0.080	0.080	0							
Al	1-81-10-09-03	3.80 3.09	3.445	21							
	1-81-10-26-03	0.749 0.769	0.759	3	0.753	0.852	88	0.723	0.290	1.060	116
B	1-81-10-09-03	28.5 28.4	28.45	0							
	1-81-10-26-03	0.722 0.733	0.728	2							
Ba	1-81-10-09-03	2.910 2.900	2.905	0							
	1-81-10-26-03	0.545 0.544	0.545	0	1.130	1.000	113				
Be	1-81-10-26-03	0.026 0.027	0.026	2	0.277	0.261	106	0.026	0.290	0.286	90
Ca	1-81-10-09-03	<0.01 <0.01	<0.01	0							
	1-81-10-26-03	<0.12 <0.12	<0.12	0	0.92	1.00	92	1,160	0.29	1,180	<0
Cd	1-81-10-09-03	1.85 1.84	1.845	1							
	1-81-10-26-03	<0.026 <0.026	<0.026	0	0.062	0.059	105	0.038	0.29	0.289	90

(continued)

TABLE 8-7 (continued)

Parameter	Record number	Splits, µg/mL			Standards, µg/mL			Spikes, µg/mL			
		Results	Average	Relative percent	Observed value	True value	Percent recovery	Original value	Spike	Original + spike	Percent recovery
Co	1-81-10-26-03	<0.080 0.082	<0.080	<0	0.366	0.348	105	0.096	0.290	0.815	27
Cr	1-81-10-09-03	4.34 4.34	4.34	0							
	1-81-10-26-03	0.261 0.260	0.261	0	0.325	0.304	107	0.272	0.29	0.542	93
Cu	1-81-10-09-03	3.25 3.29	3.27	1							
	1-81-10-26-03	0.199 0.217	0.208	9	1.04	1.00	104	0.253	0.29	0.480	78
Fe	1-81-10-09-03	15.8 16.2	16.0	3							
	1-81-10-26-03	0.071 0.070	0.070	1	0.855	0.796	107				
K	1-82-01-08-01				46.3	50	93				
	1-81-10-26-03	<6.5 <6.5	<6.5	<0							
Mg	1-81-10-09-03	3.77 3.80	3.785	1							
	1-81-10-26-03	<0.014 <0.014	<0.014	0				<0.014	0.29	0.192	<61

(continued)

TABLE 8-7 (continued)

		Splits, µg/mL			Standards, µg/mL			Spikes, µg/mL			
Parameter	Record number	Results	Average	Relative percent	Observed value	True value	Percent recovery	Original value	Spike	Original + spike	Percent recovery
Mn	1-81-10-09-03	3.77 3.80	3.785	1							
	1-81-10-26-03	0.020 0.020	0.020	1	0.517	0.478	108	0.022	0.29	0.283	90
Mo	1-81-10-09-03	12.8 12.8	12.8	0							
	1-81-10-26-03	1.62 1.64	1.63	1	1.16	1.00	116	1.89	0.29	2.15	90
Na	1-81-10-09-03	61.6 59.7	60.65	3							
	1-82-01-08-01				42.5	50	85				
	1-82-10-26-03	66.1 65.7	65.9	1							
Ni	1-81-10-09-03	13.5 13.5	13.5	0							
	1-81-10-26-03	<0.2 <0.2	<0.2	<0	0.169	0.165	102	<0.2	0.29	0.353	<53
P	1-81-10-09-03	43.3 52.8	48.05	20							
Pb	1-81-10-09-03	2.20 2.22	2.21	1							
	1-81-10-26-03	0.413 0.45	0.431	9				0.738	0.29	0.815	17

(continued)

TABLE 8-7 (continued)

Parameter	Record number	Splits, µg/mL			Standards, µg/mL			Spikes, µg/mL			
		Results	Average	Relative percent	Observed value	True value	Percent recovery	Original value	Spike	Original + spike	Percent recovery
Sb	1-81-10-26-03	<0.86 <0.86	<0.86	<0	1.05	1.00	105	<0.86	0.29	0.86	<0
Si	1-81-10-09-03	<0.025 <0.025	<0.025	<0							
Sn	1-81-10-09-03	6.47 9.63	8.05	39							
	1-81-10-26-03	<0.65 <0.65	<0.65	<0							
Sr	1-81-10-26-03	1.12 1.12	1.12	0							
Tl	1-81-10-09-03	1.53 1.50	1.515	2							
	1-81-10-26-03	0.087 0.087	0.087	1	1.02	1.00	102	0.096	0.2	0.365	93
V	1-81-10-09-03	2.85 2.7	2.775	5							
	1-81-10-26-03	<0.12 <0.12	<0.12	<0	0.912	1.00	91	<0.12	0.29	0.366	<85
Zn	1-81-10-09-03	5.48 5.8	5.64	6							
	1-81-10-26-03	<0.05 <0.05	<0.05	<0				<0.05	0.29	0.285	<81

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APPENDIX A

EXAMPLE CALCULATIONS FOR STACK GAS CONCENTRATIONS OF POHC'S TO DESTRUCTION AND REMOVAL EFFICIENCIES

Stack Gas Concentration

On 12/4/81, Run #W3-2B from bag sample collected from 0940-1045 hr, the GC/EC measured: 117 ppb chloroform (dry gas) at 25°C and 29.66 in Hg based on dynamic gas calibration standard which was factory certified to be 545 ng/min. Post-test gravimetric calibration of the permeation tube for chloroform determined the actual permeation rate of the gas standard to be 671 ng/min, or 123.1% higher. Thus:

$$117 \text{ ppb } CHCl_3 \times 1.231 = 144 \text{ ppb } CHCl_3$$

Subtracting the average baseline stack gas concentration of 75 ppb $CHCl_3$ (also corrected as above) gives:

$$144 \text{ ppb} - 75 \text{ ppb} - 69 \text{ ppb } CHCl_3$$

To convert from ppb to $\mu g/m^3$, the following equation is used:

$$\mu g/m^3 = \text{ppb} \times \frac{MW}{24.04} \times \frac{P}{P_s} \times \frac{Ts}{T}$$

where MW = molecular weight, g/mol

24.04 = molar volume of gas at 293°K and 760 torr (29.92 in Hg)

P = pressure of air sampled, torr (in Hg)

T = temperature of air sampled, °K

$$69 \text{ ppb} \times \frac{119.38}{24.04} \times \frac{29.66}{29.92} \times \frac{293}{298} = 333.97 \ \mu g/m^3$$

The volumetric flow rate of stack gas measured during Run #W3-2 was: 1,739 m^3/min (dry std.)

The emission rate, W_{out}, is then:

$$W_{out} = \frac{333.97 \ \mu g}{m^3} \times \frac{1739 \ m^3}{min} \times \frac{g}{10^6 \ \mu g} \times \frac{lb}{453.57 \ g} \times \frac{60 \ min}{hr}$$

$$W_{out} = 0.0768 \ lb/hr$$

During Run #W3-2, waste batch 3 was fed to the kiln at 3.65 gpm at 25°C. The volumetric fraction of $CHCl_3$ in waste batch 3 was 0.034 (3.4%). The density of $CHCl_3$ at 25°C is 1.4832 g/mL (kg/L).

The mass feed rate, W_{in}, of $CHCl_3$ to the kiln during Run #W3-2 was:

$$W_{in} = \frac{3.65 \ gal}{min} \times \frac{3.785 \ L}{gal} \times 0.034 \times \frac{1.4832 \ kg}{L} \times \frac{2.205 \ lb}{kg} \times \frac{60 \ min}{hr}$$

$$W_{in} = 92.172 \ lb/hr$$

The destruction and removal efficiency (DRE) is calculated as

$$\frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

The DRE of $CHCl_3$ during Run #W3-2 is:

$$DRE = \frac{(92.172 - 0.0768)}{92.172} \times 100\%$$

$$DRE = 99.917\%$$

APPENDIX B

RECOMMENDED FULL-SCALE FACILITY DESIGN AND OPERATION PRACTICES

APPENDIX B

RECOMMENDED FULL-SCALE FACILITY DESIGN AND OPERATION PRACTICES

The following section of recommendations applies mainly to an industrial kiln processing hazardous wastes on a continuous basis, rather than for a demonstration program, although most of the design recomendations could be incorporated into a well-planned demonstration burn. Prior operating experience certainly provides clearer hindsight vision. Most of the following recommendations are general for all industrial kilns which may want to burn waste fuels, but some are specific to San Juan Cement. It is anticipated that San Juan Cement will follow up the demonstration burn program with a permit application for a permanent waste storage and burning facility.

Good engineering practice and safety cannot be separated in the handling of flammable, toxic hydrocarbon liquids and must be included in the design and review of any hazardous waste handling system.

B-1 TANK TRUCK UNLOADING AND STORAGE TANK MODULE

Hazardous fluid unloading and transfer operations offer one of the highest likelihoods of accidents; i.e., fire, spills, or worker exposure. Technical bulletins of the Chemical Manufacturers Association (CMA) and the American Petroleum Institute (API) provide excellent guidance for the unloading of tank trucks [35-38]. Some of the procedures which can be used to prevent a hazardous unloading situation are:

(1) The condition of the cars is examined, and any leaks are to be reported immediately.

(2) Before unloading starts the area is checked to be sure it has no exposed lights, fires, or other sources of ignition.

(3) Vents on tankers are protected by flame arresters.

(4) In all cases, personnel should be thoroughly trained and have been given written instructions specific for each material they will handle. This should become a permit requirement that the company will be required to have especially trained

and authorized personnel at the waste storage and pumping site for unloading and storage of waste fuels [1].

(5) Adequate personal, protective equipment has been furnished for those involved in the loading and unloading of tankers. For materials that are corrosive to the skin or that may be absorbed through it, full protective clothing with face masks, rubber gloves, rubber shoes, etc., is required. When materials that have toxic vapor or gas are unloaded, personnel should be equipped with airline respirators or self-contained breathing equipment. Protective equipment not available at the site should be obtained even though this may mean some delay in making the transfer.

(6) First aid and medical procedures are worked out in advance and posted in the unloading area. Where unusually toxic substances are handled, on-site medical personnel will have information on the characteristics of the material and on the medical management needed for any material they may encounter.

(7) Fire extinguishers of adequate type for the material handled are distributed throughout the area.

(8) Personnel responsible for unloading stay in the immediate vicinity of the operation at all times, and ascertain that all conditions are normal.

(9) An emergency shower and an eyewash device is available at each loading location. Preferably, these devices are tied to an alarm system that would bring help to anyone making use of them.

(10) Safe access to the top of the vehicle is one general safety requirement for liquid unloading. This is particularly important for top unloading, but it may also be necessary for operations such as gauging or sampling. Thus, loading racks with suitable ladders, platforms, gangways, or even railings permanently affixed to the vehicle are usually required.

(11) Keeping liquid-unloading facilities usable in adverse weather conditions, such as rain or icing, may be difficult, but every effort must be made to keep them safe. Good general illumination, especially at night, is far preferable to providing the operator with an extension light, which he might drop.

(12) Steel pipe and swing joints or flexible hose of the standard metal type are usually used for connections to tank trucks. Metal-reinforced rubber hose of a type resistant to the material being handled is acceptable but less desirable.

(13) Each line and connection should be clearly identified to avoid intermixing materials.

(14) A totalizing flow meter should be installed to record the quantities of waste fuel handled during any unloading or loading.

(15) Pumps are preferably located outdoors so that fire at the pump will not expose property of appreciable value. They should not be located inside diked areas. Pumps are sometimes located in small detached noncombustible pump houses or in cutoff rooms of main buildings. When they are located indoors and handle flammable liquids with flash points below 43°C (110°F), positive low-level exhaust ventilation of 5.08×10^{-3} $m^3/s/m^2$ (1.0 cfm/ft^2) of pumproom floor area is recommended. Natural ventilation is acceptable for less hazardous liquids.

(16) Where flammable liquids are handled in a pump house, motors can be partitioned and sealed off from the rest of the pump house, or can be of a type approved for use in flammable atmospheres. It is a good operating and safety practice to have a well-marked master cutoff switch outside the building. However, consideration is normally given to locating flammable liquid pumps outside of buildings whenever feasible.

(17) As a fail-safe precaution, an interlocked warning light or physical barrier system is often provided in unloading areas to prevent vehicular departure before complete disconnect of flexible or fixed transfer lines.

(18) A closed vapor line between the storage tank vents and the tank trucks should be provided to return the displaced volatile organic vapors from the storage tanks to the tank truck, when loading the tanks.

(19) In conjunction with condition (18) to control organic emissions, a back-up carbon adsorption vapor control system should be provided to control volatile organic compound storage tank breathing emissions.

(20) A management control and recordkeeping system should be established identifying the source, chemical composition, and quantity of all waste materials received for destruction. This management and recordkeeping system may be submitted to the environmental control agency for review and approval prior to initiating any liquid waste storage or destruction. Such records should be available for inspection by the environmental control agency at all times [1].

(21) Sometimes waste storage tanks are loaded into tankers; e.g., to repair a tank or replace valving. The unloading system should be plumbed to operate in reverse for these cases, and all of the above design recommendations should also apply.

(22) The waste fuel should be screened (sieved) before storage to remove large solids.

Spill and Runoff Containment

Drainage from the unloading area is collected or diverted to allow runoff of any spills or runoff from rainfall to permit recovery or at least proper disposal. The basic objective of secondary containment is to prevent the discharge of hazardous materials to waterways, sewer systems, or groundwaters. Containment systems which fail under rainstorm conditions are considered inadequate. To the extent feasible, such containment is designed to hold 110% of the largest unit handled (or largest unit contents plus the maximum 24-hr/10-yr rainfall event, if greater).

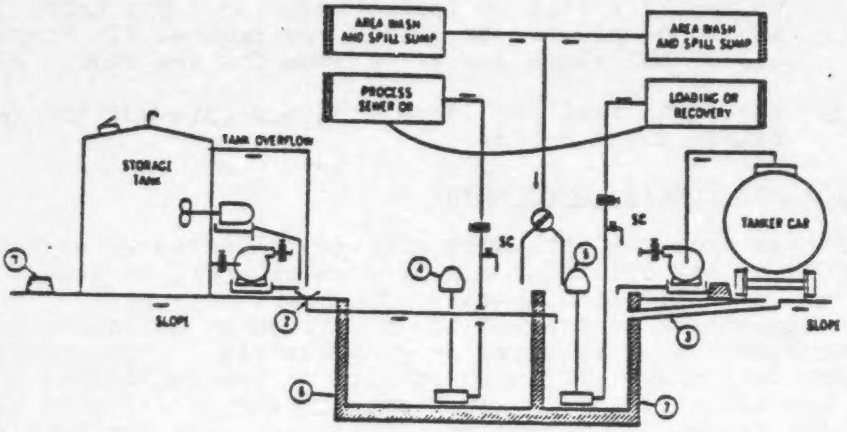
For tank trucks a system of containment curbs is used for unloading areas, using ramps to provide truck access into the confines of the containment curb.

A lined trenching system encompasses the railroad tank car unloading area. The trench is designed to carry away any spill or runoff to a catchment basin or holding pond for later treatment. Figure B-1 illustrates a containment curb type spill catchment system, depressed area form.

Static Electricity Prevention

Static electricity is generated when fluid flows through a pipe or from an orifice into a tank. The principal hazards created by static electricity are those of fire and explosion, which are caused by spark discharges containing sufficient energy to ignite any flammable or explosive vapors or dust present. A point of great danger from a static spark is the place where a flammable vapor may be present in the air, such as a delivery hose nozzle.

The terms "bonding" and "grounding" often have been used interchangeably because the terms are poorly understood. Bonding is done to eliminate a difference in potential between objects. Grounding is done to eliminate a difference in potential between an object and ground. Figure B-2 illustrates bonding and grounding of a tanker during a loading (or unloading) operation. For detailed information consult NFPA Standard No. 77, "Recommended Practice on Static Electricity."


AREA WASH AND SPILL SUMP
AREA WASH AND SPILL SUMP
PROCESS SEWER OR
LOADING OR RECOVERY
STORAGE TANK
TANK OVERFLOW
TANKER CAR
SC
SC
SLOPE
SLOPE
1
2
3
4
5
6
7

ITEM	DESCRIPTION OF PROTECTION	OPERATION/EQUIP. PROTECTED	HAZARD
1	DIKE	TANKS	SPILLS, WASHING
2	RAISED DRAIN	OVERFLOW, DRIPS	CONC. SPILLS
3	TRENCH DRAIN	TANKCAR	UNLOAD, SPILLS
4, 5	SUMP PUMP	PROCESS SEWER	SLUG DISCHARGE
6	DILUTE SUMP	TANK MAT	SPILLS
7	CONC. SUMP	PROCESS SEWER	DISCHARGE

Figure B-1. Containment curb type spill catchment system, depressed area form [4].

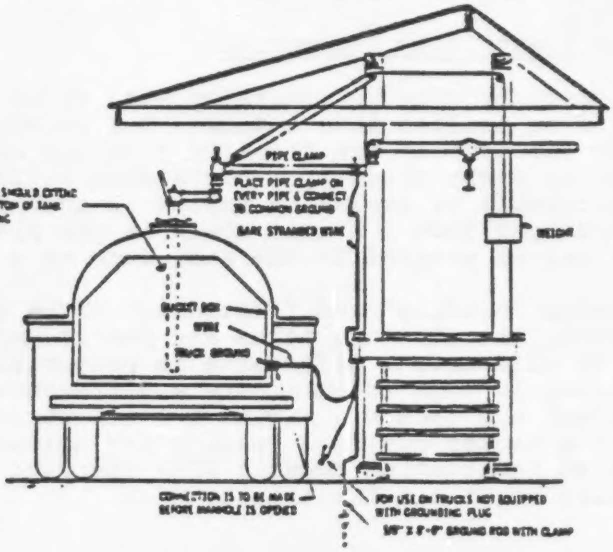

DOWNSPOUT SHOULD EXTEND TO NEAR BOTTOM OF TANK WHEN LOADING
PIPE CLAMP
PLACE PIPE CLAMP ON EVERY PIPE & CONNECT TO COMMON GROUND
BARE STRANDED WIRE
WEIGHT
BUCKET BOX
WIRE
TRUCK GROUND
CONNECTION IS TO BE MADE BEFORE MANHOLE IS OPENED
FOR USE ON TRUCKS NOT EQUIPPED WITH GROUNDING PLUG
5/8" X 8'-0" GROUND ROD WITH CLAMP

Figure B-2. Bonding and grounding of a flammable liquid tank truck and loading rack [4].

Waste Fuel Storage

The storage tank farm facility is designed for waste fuels which will probably have components with high vapor pressure, will be corrosive, will contain suspended solids, and may polymerize. Tanks may have to be provided with nitrogen blanketing. Before storing, the suspended solids should be removed to minimize equipment erosion/corrosion and valve sticking. Tank access should be designed to facilitate entry for cleaning and inspection.

Any nearby fugitive particulate emission source, such as product loadout, storage pile moving, or dusty truck traffic will have to be well controlled to minimize equipment problems due to dust accumulation in or near the waste fuel storage area.

Both vertical and horizontal tanks are available for waste fuel storage. Vertical tanks are more economical to install and occupy less space, while horizontal tanks are easier to maintain and repair. Usually the lower maintenance generally required by horizontal tanks does not offset their higher cost and greater space requirements; hence, vertical tanks are normally recommended. If, however, it appears that future compartmentalization of the tank will be likely (as with segregated waste storage), it is easier to modify a horizontal tank.

Tanks should not knowingly be used if the "head" or "top" is in a corroded-through condition. Action is taken to drain such tanks and repair the defective member as promptly as possible.

An excellent waste fuel storage tank design for cement kiln plants is a vertical carbon steel tank, cone-top, fixed-roof, with a concave bottom. The tanks(s) should be placed on 6 inches of sand rather than a concrete pad, because the area near cement kilns experiences vibrations from the rotary kilns. A concave bottom allows for more complete tank emptying and will facilitate maintenance cleaning.

Depending upon the liquid waste contained, tank storage can also require many accessory equipment features such as:

(1) Flash arrester fill pipes.

(2) Flame arrester rodding and sampling units.

(3) Conservation breather vents with pipe-away construction--used where pressure or vacuum relief is required and vapors must be piped away rather than released into the atmosphere.

(4) Tank vent condensers--designed to condense and return to the tank vapors that could escape, as shown in Figure B-3. Due to potential unanticipated reactions between physically or chemically incompatible wastes, large volumes of organic vapor can be generated and must be vented to some control device. Venting the tanks into the incinerator combustion air intake has the potential of creating an explosive condition, even with nitrogen blanketing. Chilled water condensers, coupled with knockout tanks, are best utilized to control emissions from the liquid transfer and storage facilities [39].

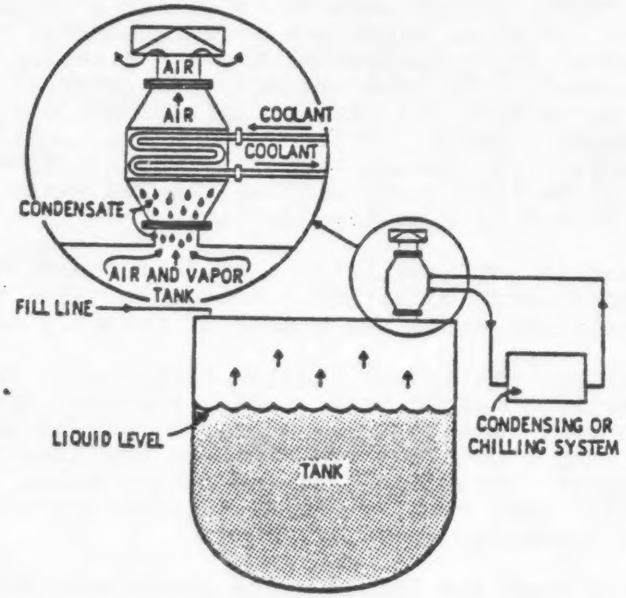


Figure B-3. Typical tank condenser vent system.

(5) Manhole and emergency pressure relief vent covers--to provide emergency pressure relief as well as access for tank cleaning.

(6) Internal safety valve--intended for use where tanks are required to be equipped with valves that close automatically when subjected to fire.

(7) Integral internal heating coils--usually steam, designed to prevent freezing of tank contents, if necessary.

(8) Overflow piping--usually connected to an adjacent tank to mitigate spill possibilities.

For safe facility design in the whole storage area, provisions should be considered and made to protect personnel and the immediate environment from catastrophe--particularly fire hazards and material spills. The waste fuels at an industrial kiln should be stored in an isolated area of the plant, preferably well fenced and locked, to provide security from unauthorized personnel and vandals.

Fire Safety

Volume 1 of National Fire Codes [National Fire Protection Association (NFPA), Boston] contains recommendations and standards in NFPA 30, "Flammable and Combustible Liquids Code," for venting, drainage, and dike construction of tanks for flammable liquids. Also possibly applicable are NFPA 327, "Standard Procedures for Cleaning or Safeguarding Small Tanks and Containers," and NFPA 43A, "Liquid and Solid Oxidizing Materials."

Many of the devices and equipment utilized to prevent fire hazards at the storage tank were discussed. Some other considerations which may apply to storage of large quantities of flammable liquids include:

(1) Instrumentation or remotely-operated valves to minimize flow of flammables.

(2) Combustible gas monitors in the storage area which have an alarm set at 25% of the lower flammable limit.

(3) Combustible gas monitors that automatically actuate a deluge system or safely shut down systems below lower flammable limit.

(4) Drainage and collection ponds (equalization basins) to carry away liquid spills resulting from a fire incident.

B-1.5 Spill/Toxicity Safety

The most effective way of addressing a bulk liquid storage area's vulnerability to spill incidents is to prevent them from happening. Assuming that all storage tanks are properly designed, equipped with overflow alarms, and used only for intended or compatible purposes, the possibility of spills can be substantially reduced by:

(1) Assuring the continual physical integrity of the vessels and their fittings (inspection and testing).

(2) Establishing strong administrative controls covering all loading/unloading and in-plant transfer operations (plans and procedures).

(3) Providing adequate secondary containment facilities (dikes, diversion ditches, equalization basins).

Physical Testing and Inspections--Spark testing (of lined storage tanks), wall-thickness testing, or other appropriate means of non-destructive physical testing or inspection should be conducted on storage vessels which hold hazardous liquids.

The exterior of each bulk storage tank should also be visually examined at regular intervals. Each inspection is to include an examination of seams, rivets, nozzle connections, valves, and pipelines directly connected to the tank. Visible leaks of waste from tank seams and rivets should be then promptly corrected. Foundations and/or tank supports are also subject to inspection.

Liquid Level Sensing--New and old tank installations should be, as far as practical, fail-safe engineered, or updated to a fail-safe engineered installation. Design considerations can be given to providing the following devices:

(1) High liquid-level bell or horn alarms with an audio signal at a constantly manned operating or listening station; in smaller plants an audible air vent may suffice.

(2) Low liquid-level alarms with an audio signal at a constantly manned operation or listening station; such alarms can also have a non-bypassing reset device that can be readjusted to a given operating level following tank fill or liquid removal.

(3) High liquid-level pump cutoff devices set to stop flow at a predetermined tank content level.

(4) Direct audible or code signal communication between the tank gauger and the pumping station.

(5) At least one fast response system for determining the liquid level of each bulk storage tank such as digital computers, telepulse, or direct vision gauges.

As a result of the documentation and analysis of spill incidents, the need for research in the area of fail-safe, level-sensing devices was recognized as one aspect of the tank overflow problem, the others being personnel errors and defective or missing gauges. An EPA research project was conducted which involved the testing and evaluation of representative devices in actual use conditions.

It was recognized that many manufacturers of material level sensors provide excellent equipment. Some of these devices are indicators only, other devices actuate alarms and switches, and others are connected in a fail-safe mode to prevent over-fills.

The general scope of the work for the EPA Contract "Development/ Demonstration of Fail-Safe Devices for the Preventing of Spills of Hazardous Materials During Production and Storage" consisted of [40]:

(1) Assessing the current technology;

(2) Conducting laboratory- and pilot-scale development, modification and demonstration, if necessary;

(3) Constructing, installing and demonstrating the devices or equipment under actual, full-scale, regular use conditions.

To meet these requirements, it was necessary to critically evaluate the equipment for operational and maintenance characteristics, reliability, ease of installation, availability of service and parts, cost, estimated longevity, vulnerability to environmental hazards both inside and outside the vessel, availability of explosion-proof construction, methods of corrosion protection, availability of fail-safe configurations, etc. By assigning weighted numerical values to the various characteristics of the level-sensing devices a figure of merit was determined.

An in-plant case study was conducted for the type of storage represented by a spent solvent tank, in which the liquid level was to be fail-safe monitored and controlled. In this situation, two problems had plagued previously used measuring devices: an extremely corrosive environment and sludge buildup in the tank bottom. These problems will be very analogous to the problems associated with storage of waste fuels at industrial kiln facilities.

The sensor chosen for testing was a Brooks Maglink unit (Model 5320-GTG-D). It was operated by a donut-shaped, polypropylene float captive on a Teflon-coated, stainless steel guide tube. The float is coupled magnetically to a follower in the guide tube which, in turn, is connected to the transmitting head, varying the output air pressure from 21-103 kPa (3-15 psi) depending on the elevation of the liquid surface. When the solvent tank is nearly full, the pressure output operates a pressure switch, cutting off power to an existing solenoid valve which, in turn, cuts off an air supply to a spring-loaded, pneumatic fill valve causing it to close.

The test panel board with the fail-safe configuration and recorder is connected to the Brooks Maglink unit in series with the existing pressure switch. Two pressure switches are arranged on the test panel board with high and low settings, each of which will cut off a simulated fill mechanism. The low cutoff point is below the low output of the Brooks unit, making the system fail-safe in the event of pneumatic pressure loss.

The Brooks Maglink unit with the pneumatic head was set up and checked out in the Laboratory upon its receipt. The output was linear throughout the range and the dial on the transmitting head was accurate to one tenth of one percent.

Tank Overfill--A variety of engineering practices suited to the nature of any hazardous material stored are used to prevent tank overfilling, a major source of spill incidents. The following general principles can be used in designing a system of protection against tank overfill:

(1) Tanks are gauged before filling.

(2) Overflow pipes are connected to adjacent, compatable waste storage tanks, or to secondary containment.

(3) Fail-safe devices and level alarms have been tested and insured in place.

(4) Provisions to prevent static electricity discharge have been implemented.

Protection of Integral Heating Coils--Many liquids in storage require auxiliary heating to remain in a fluid state. This is normally accomplished economically by integral steam coils inside the storage tank and, often, agitation.

To control leakage through integral heating coils which may become defective through prolonged use, the following design factors are considered and applied:

(1) The past life span of internal steam coils is determined, and a regular system of maintenance and replacement that does not exceed the anticipated life span is established.

(2) The temperature and environment is carefully considered when selecting heating coil materials to reduce failure from corrosive action, prolong life, and reduce replacement costs.

(3) The steam return of exhaust lines from integral heating coils which discharge into an open watercourse is monitored for contamination, or passed through a settling tank or skimmer, etc.

(4) The nature of the wastes is carefully considered to prevent wastes from caking on the heating coils, which reduces their efficiency as well as causing waste materials to be contained in a tank thought to be empty.

(5) The feasibility of installing an external heating system is also considered, and, if feasible, often is recommended to solve problems which may arise from implementation of (1) through (4).

Secondary Containment--All bulk storage tank installations at a hazardous waste incineration facility should be planned so that a secondary means of containment is provided for the entire contents of the largest single tank. Dikes, containment curbs, and pits are commonly employed for this purpose, but they may not always be appropriate. An alternative system would consist of a complete drainage trench enclosure arranged so that a spill could collect and be safely confined in an in-plant catchment basin or holding pond.

Dikes are generally constructed of concrete, cinder blocks, and/or earth. However, dike materials should be designed to be chemically resistant and essentially impervious [e.g., permeability rate no greater than 10^{-7} cm/s when subjected to a head of 0.305 m (1 ft) of water] to the substances contained. Acceptable engineering design criteria for a dike will enable it to withstand a sudden massive release.

Some of the important design guidelines for dike construction include [41]:

(1) Single storage tank -- The capacity of diked area is at least adequate to hold the entire tank contents plus a reasonable allowance for precipitation. Local regulations may contain more stringent requirements. An alternative design goal is for the diked area to contain the volume of the tank plus 0.3 m (1 ft) of freeboard.

(2) Clustered storage tanks -- The capacity of the diked area is adequate to hold the entire contents of the largest tank plus a reasonable allowance for precipitation. Again, local regulations may be more stringent.

(3) To the extent feasible, dike walls generally do not exceed a height of 1.8 m (6 ft) above interior grade. A greater height might require the observance of tank entry procedures including safety harnesses, oxygen deficiency checks, standby observers, and other precautions each time it is necessary to enter the diked area.

B-2 WASTE PUMPING AND RECIRCULATION MODULE

In general, two design options exist in choosing a type of feed pump: (1) positive-displacement pumps or (2) centrifugal pumps. It has been shown in this program that feed-line pressures over 1,030 kPa (150 psi) are unnecessary, so either type of pump will suffice.

Positive-displacement pumps have, as their principle of operation, the displacement of the liquid from the pump case by reciprocating action of a piston or diaphragm, or rotating action of a gear, cam, vane, or screw. The type of action may be used to classify positive-displacement pumps as reciprocating or rotary. When a positive-displacement pump is stopped, it serves as a check valve to prevent backflow.

Centrifugal pumps operate by the principle of converting velocity pressure generated by centrifugal force to static pressure. Velocity is imparted to the fluid by an impeller that is rotated at high speeds. The fluid enters at the center of the impeller and is discharged from its periphery. Unlike positive-displacement pumps, when the centrifugal type of pump is stopped there is a tendency for the fluid to backflow.

Pump Emission Control

Operation of various pumps in the handling of fluids can result in the release of environmental contaminants. Both reciprocating and centrifugal pumps can be sources of emissions.

The opening in the cylinder or fluid end, through which the connecting rod actuates the piston, is the major potential source of containants from a reciprocating pump. In centrifugal pumps, normally the only potential source of leakage occurs where the drive shaft passes through the impeller casing.

Several means have been devised for sealing the annular clearance between pump shafts and fluid casings to retard leakage. For most applications, packed seals and mechanical seals are widely used.

Packed seals have been used on both positive displacement and centrifugal-type pumps. Typical packed seals generally consist of a stuffing box filled with sealing material that encases the moving shaft. The stuffing box is fitted with a takeup ring that is made to compress the packing and cause it to tighten around the shaft.

Lubrication of the contact surfaces of the packing and shaft is effected by a controlled amount of product leakage to the atmosphere. This feature makes packing seals undesirable in applications such as with waste fuels where the liquid can cause a pollution problem.

The second commonly used means of sealing is the mechanical seal, which was developed over a period of years as a means of reducing leakage from pump glands. This type of seal can be used only in pumps that have a rotary shaft motion. A simple mechanical seal consists of two rings with wearing surfaces at right angles to the shaft. One ring is stationary while the other is attached to the shaft and rotates with it. A spring and the action of fluid pressure keep the two faces in contact. Lubrication of the wearing faces is accomplished by a thin film of the material being pumped. The wearing faces are precisely finished to ensure perfectly flat surfaces. Materials used in the manufacture of the sealing rings are many and varied. Choice of materials depends primarily upon properties of fluid being pumped, pressure, temperature, and speed of rotation. The vast majority of rotating faces in commercial use are made of carbon.

An excellent mechanical seal for centrifugal pumps is the Chesterton double cartridge seal with Kelrez® O-rings. When the front seal fails, then a weep hole indicates failure (dripping) and the second seal takes over. This type of seal is initially expensive, but the cartridge can be returned and rebuilt.

Emissions to the atmosphere from centrifugal pumps may be controlled in some cases by use of the described mechanical-type seals instead of packing glands. For cases not feasible to control with mechanical seals, specialized types of pumps, such as canned, diaphragm, or electromagnetic, are required.

Another specialty category is the sealed pump, which has no external seal or potential leakage. The two major types are the canned-rotor and the magnetic. Sealed pumps are used where no leakage can be tolerated, or where pump seal failure might cause major trouble. Such pumps are available in a limited range of sizes, most are low-flows, and all are of single- or two-stage construction. They have been used for both high-temperature and very low-temperature liquids. High-suction-pressure applications avoid the need for a troublesome high-pressure stuffing box. The centrifugal-type pumps follow the same hydraulic performance rules as conventional centrifugal pumps. Because of their small size, these pumps show a rather low efficiency but, in dangerous applications, efficiency must often be sacrificed for safety.

Pump and Piping Safety

The primary objectives of pumping and piping systems are to prevent escape of liquid and to keep to a minimum the quantity lost if the liquid does escape. Inherent safety and freedom from human failure can, to a considerable extent, be built into a hazardous/flammable liquid system. Some design recommendations which help to attain the above objectives are listed below:

(1) Complete automatic sprinkler protection is provided in indoor areas where pumps, piping, tanks, and other parts of hazardous liquid transfer systems are located. In well-drained areas, sprinkler discharge of 2.04×10^{-4} $m^3/s/m^2$ (0.30 gpm/ft^2) of floor area is usually recommended to prevent structural and equipment damage.

(2) Indoor piping is located either overhead or in trenches in the floor. Overhead piping is normally installed close to ceilings or beams or along walls at least 1.8 m (6 ft) above floor level. If piping is located in a trench in the floor, the trench is covered with removable steel plates and a trapped drain installed to a point of safe discharge. Positive-exhaust ventilation is provided in the trench, or the trench is backfilled with sand for liquids having closed-cup flash points below 43°C (110°F).

(3) Provisions are made to clean out the piping and equipment when long or scheduled shutdowns occur. This is usually done by purging with steam. The condensate is then collected and treated as a wastewater.

(4) Pipe materials are used which are chemically resistant to the liquid handled, which have adequate design strength to withstand the maximum service pressure and temperature, and which, when possible, are resistant to mechanical damage or thermal shock. Cast-iron, soft-rubber, or thermoplastic pipe or fittings of low melting point are never used.

(5) Each waste material pipeline is clearly marked by lettering (coded or otherwise), color banding, or complete color coding to indicate the product transferred therein. The coding normally conforms with company policy or standard plant practice which, in turn, should conform with state or federal requirements.

(6) Each hazardous material product-fill line which enters a tank below the liquid level has a one-way flow check valve located as closely as possible to the bulk storage tank. In addition to confining the product to the tank, in the event of valve or pipeline failure, the check valve permits overhaul of the main shut-off valve and should aid in preventing shock loading of the pipeline and valves from a "slug" of the tank content caused by backflow into an empty fill line. The waste feed flow in suction lines should be controlled by use of a positive shutoff valve; e.g., ball valve.

(7) Buried pipelines are generally avoided. When they do occur however, buried installations have a protective wrapping and coating and are cathodically protected if soil conditions warrant. A section of the line is then exposed and inspected regularly. This action is normally recycled until the entire line has been exposed and examined on a regularly established frequency. An alternative would be the use of exposable pipe corridors or galleries.

(8) When a pipeline is not in service, the terminal connection at the transfer point is capped or blank-flanged, and marked as to origin.

(9) Wood-to-metal is normally avoided as a pipeline support since it is apt to retain moisture and cause pipeline corrosion which, when coupled with the abrasive action caused by the pulsating action of the line, could cause line failure with resulting leakage. Supports are generally designed with only a minimum point of surface contact that allows for the pulsating movement (expansion and contraction). During inspections the general condition of items, such as line welds, flange joints, valve glands and bodies, catch trays, pipeline supports, locking of valves, and metal surfaces, are assessed.

(10) Elevated pipelines are also subjected to constant review to insure that the height of vehicular traffic granted plant entry does not exceed the lowermost height of the elevated line; gate check-in and in-plant travel are routes which warrant attention in this respect.

(11) As far as possible, feed pumps are located as close as possible to the storage tanks, but not within the diked area. If a feed pump system is to be located within the diked area it must have an explosion-proof design motor drive, e.g., air-driven or XP electric motor, and be located so a trapped spill or stormwater will not submerge the pump.

Line Filtering

Several stages of waste fuel line filtering are recommended before the feed pump system in order that the pump, control valves, and measuring devices enroute to the burner nozzle do not stick or clog. In a waste mixture, solid particulate may even form as precipitates or polymer seeds *in situ*. To minimize these conditions, strategically placed screens and filters in sequence and redundant are recommended in maintaining onstream time.

Recirculation

A waste fuel feed system will have recirculating loops installed, chiefly to relieve excess feed pump pressure and to keep any solids remaining in the waste fuel mixture from settling. Recirculation lines to the storage tanks must be equipped with dip tubes to minimize static electricity buildup. Bonding and grounding between the feed pump system and the storage tank are also recommended. Two or more recirculation loops may need to be installed; Figure B-4 illustrates an example of multiple recirculation.

B-3 FLOW CONTROL AND MONITORING MODULE

An automated instrumentation system should be used to transfer waste fuel from storage to the kiln. Electrical and/or pneumatic systems should be installed to permit observation of control, from a graphically illustrated control panel which shows such

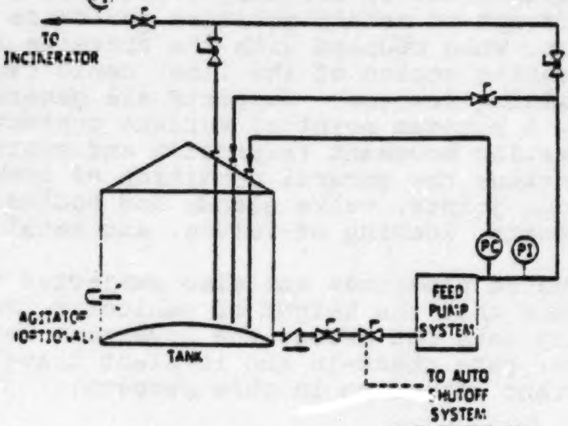


Figure B-4. Liquid feed system with redundant recirculation.

things as discharge valve positions, pump motor operation, storage tank levels (high and low), storage tank agitator operation, and liquid or solid waste flow. The control instrument technology has been well developed. Instrumentation such as that already used in oil-burning cement plants is excellent. The difficulty encountered in the hazardous waste liquid application is caused by the nature of the product. It is invariably corrosive, contains particulate, and has a nasty tendency to foul the surfaces it contacts. The flow-sensing system is the heart of the control problem [42]. Materials of construction for all sensors must be carefully chosen.

Some important process monitoring recommendations in designing an applicable instrumental control system are [1]:

(1) The kiln should be operated at all times in an oxidizing atmosphere. Oxygen in the kiln exhaust gases will be maintained at a level of not less than 0.25% and continuously recorded.

(2) No waste liquid burning should take place unless the cement kiln is operating at normal temperatures in the range of 1,260°C to 1,660°C (2,300°F to 2,800°F) as a kiln flame temperature. The waste liquid materials should be injected directly into the kiln fuel flame. Instrumentation should be provided to continuously record the rate of flow of these wastes. Burning should not be permitted during periods of kiln startup, shutdown, major upset, or fuel interruption.

Kiln coating temperature will be measured by a recording optical pyrometer and coal or oil fuel flow should be continuously measured and recorded.

(3) System controls should provide for automatic shutdown of introduction of waste liquid materials into the kiln in the event any of the following conditions occur:

   (a) Cement kiln temperatures fall below 1,200°C (2,200°F),

   (b) Coal or fuel oil flow interruption,

   (c) Kiln speed decrease to below 60 revolutions per hour,

   (d) Loss of draft in the firing hood,

   (e) Exhaust gas oxygen content less than 0.25%.

(4) If the outside skin temperature of the kiln exceeds 480°C (900°F), the feed of waste liquid chemicals should be shut off from introduction into the kiln, and shutdown should be initiated for repair of the refractory. Reintroduction of chemical waste liquids should not take place until such lining repairs are completed. (This is to prevent HCl attack of the steel kiln shell.)

(5) Chemical waste liquid introduction into the kiln should cease in the event of mid-kiln clinker ring formation. Reintroduction of chemical waste liquids into the kiln should not take place until such ring is eliminated. Clinker ring formation at the end of the kiln may or may not require shutoff of the waste fuel depending on operator judgment. Successful clinker ring breakage did occur when burning hazardous waste.

(6) Automated monitors should be employed to alert operators in the event of a waste-fuel handling problem. A pressure transducer located in the waste piping at the entrance of the kiln should be provided to automatically turn off the waste fuel pump in the event of a sudden pressure drop due to pipe rupture or pump failure.

(7) Interlocks should be provided to automatically stop the flow of waste fuels if either normal fuel supply or combustion air flow are interrupted.

(8) Monitoring systems capable of detecting volatile organic vapors should be placed at key process locations to signal accidential waste fuel leaks. Periodic monitoring for volatile organic compound emissions should be provided.

Backup/Redundancy Provisions

The functional diagram of a waste fuel incineration facility indicates that most components of the system are in a "series" configuration; each series component must be adequately functioning to avoid degraded performance. A few process components may be in a "parallel" configuration allowing a switchover to another component when problems are detected with an on-stream component. Examples are waste feed line filters which will usually have two or more units in parallel. Critical thermocouples for temperature measurement related to control functions and automatic shutoff must be redundant. Feed pumps are typically redundant.

Redundant storage tank level monitors are recommended. At the minimum, tank access for the age-old method of dip stick level gauging should be provided as a backup.

Flow monitoring cells need backup devices to assure safety and accurate recording of waste fuels consumed for manifest purposes. At least two flow rate measuring devices capable of calibration are recommended plus a fuel flow totalizer.

Valving and Control Safety Consideration

Valve selection requires consideration of three basic and critical details:

(1) The flow control element

(2) The regulating mechanism

(3) The seal to contain the fluid within the valve.

In addition to these three important design aspects, features such as mechanical strength, materials of construction, dimensional arrangement, and types of end-connections are considered.

Valves are weak links in fluid transfer systems as regards leaks and fugitive emissions. There are three possible types of leakage:

(1) Waste fuel escapes downstream, past flow-control element in closed position. Identified as "flow seal" leakage.

(2) Waste fuel escapes to the outside of the valve, from around the stem and from the joints (bonnet) with the body. Identified as either stem-seal or bonnet-seal leakage.

(3) Air leaks into the valve body and to the waste fuel under vacuum.

Safety Shutoffs--Hazardous and flammable-liquid pumping and piping systems should be equipped with emergency shutoffs to stop the flow of liquid in event of fire or accidental escape of liquid or vapor. This can usually be done by safety shutoff valves and/or positive-displacement pumps. In general, these devices are arranged for automatic operation in event of fire and for manual or automatic operation in event of accidental escape of liquid. If a fire could occur anywhere at an installation, provision for remote actuation of the main safety shutoff valve will be needed.

(1) Safety shutoff valves are needed in flammable-liquid systems in the following locations:

  (a) At connections on supply and feed tanks where transfer is by centrifugal pump or other means that permit the maintenance of continuous pressure in the system. The possibility of siphon action through a centrifugal pump requires installation of a safety shutoff valve on the pump inlet.

  (b) On feed lines where they enter important buildings or structures or on branch lines where they take off from main-supply headers. The valve is located out of doors or immediately adjacent to an exterior wall, accessible from outdoors.

  (c) On feed lines at dispensing locations, e.g., branching to more than one kiln.

(2) Safety shutoff valves may be of the diaphragm, solenoid, or weight- or spring-operated fusible-element types. They generally should incorporate some of the following design features:

  (a) Have bodies with the appropriate service rating for the maximum pressure and temperature to be encountered. Bodies should be of carbon steel or black iron; brass is unacceptable.

  (b) Close on failure of the operating electrical or air supply.

  (c) Close in the direction of the liquid flow so that system pressure tends to hold the valve in the closed position.

  (d) Close against a pressure of at least 150% of design rating.

  (e) Close within 5 seconds after actuation.

  (f) Valve should not readily be bypassed, blocked, or otherwise made ineffective.

(g) Have an indicator to show when the valve is open or shut, except on packless solenoid types.

(h) Be manually reset, except where the valve-control circuit is arranged for manual resetting.

(i) Have no direct connections between the liquid and air section of diaphragm valves that might permit leakage of the liquid past the packing into the air lines.

(j) Have packing and lubrication, if any, resistant to the liquid being handled.

(3) Automatic operation of safety shutoff valves and/or direct-displacement pumps is normally accomplished by one of the following methods:

(a) Actuation by thermal devices located at the ceiling and above the point of flammable-liquid use where spills may be expected.

(b) Release of a dead-man control.

(c) Operation of the fire-protection system. With automatic sprinkler systems, actuation may be by waterflow indicators, alarm valves, or dry-pipe valves with hydraulic-pressure switches. With special fixed extinguishing systems, actuation is by pressure switches. Drain and alarm tests of sprinkler system are made during idle periods or arranged that they can be made without operating the safety shutoff.

(d) If the piping contains fragile components such as rotameters, the safety shutoff is actuated automatically by excessive pressure drop downstream from such components.

(4) Arrange safety shutoff valves and/or positive-displacement pumps for manual shutdown by use of one or more stop buttons or switches at safe and accessible locations throughout the flammable-liquid system. In general, such stop buttons or switches are located near points of egress from the building or structure.

(5) Self-closing manual valves and dead-man controls of a type not readily blocked open are recommended as emergency safety shutoffs on small systems, where liquid transfer is intermittent, and on larger systems that lend themselves economically to such an arrangement. They require constant attendance by the operator and close automatically if he leaves.

Gages, Meters, and Gage Glasses--

(1) Accessories on waste fuel piping systems, such as gages, meters, gage glasses, hydrometers, and sight glasses are designed to have strength equal to that of the piping system.

(2) Gage glasses are particularly susceptible to breakage. Their use is discouraged.

(3) Restricted orifices should be used in piping to gages and instruments to reduce the amount of leakage in event of failure.

(4) Armored rotameters or instruments that read indirectly or sample a proportion of the flow in preference to those that enclose the entire stream or have the full flow directed to the glass reading chamber are also preferred.

Operating Controls--

(1) Operating control valves are located in hazardous and flammable-liquid piping systems so as to regulate the control and flow of liquids to connected equipment and to isolate equipment for maintenance purposes. Conventional types of valves are suitable for most waste fuels. Valves used should have having the appropriate service rating for the maximum pressure and temperature to be encountered and packing or lubrication resistant to the liquid being handled.

(2) Valving is arranged to minimize the likelihood of improper operation. Rising-stem or other valves that indicate whether open or closed are preferred. The following recommendations for valve arrangements should be generally followed where applicable:

    (a) Two ball valves rather than a three-way valve should be used at all branch lines so that flow can be easily determined and positive shut-off to all lines obtained.

    (b) Electrical or mechanical interlocks are provided between valves so that the position of one valve with respect to another will be automatically determined.

(3) Hydraulic accumulators or safety relief valves are provided on pipelines that can be valved off with liquid trapped between valves. This prevents damage or overpressure from thermal expansion. The discharge is piped from safety relief valves to a collection point.

(4) If control valves are to be remotely actuated, valves are chosen having characteristics described in recommendation 2 of Safety Shutoffs and arranged for operation in an emergency situation.

Preplanning of the proper operation of a hazardous waste incineration facility is necessary to protect and prevent adverse effects of the facility on the public health or to the environment. Proper facility operation, on a day-to-day basis, includes plans and manuals of operation for handling wastes, safety at the site, monitoring of operating parameters, monitoring to assure protection of the operating company and operator training. These plans are developed within the operating company (and corporate structure) and are done in cooperation with other neighboring or similar organizations and with governmental agencies. It may not always be possible for all of them to fully cooperate or participate, but through planned action each organization is made aware of certain available assistances.

B-4 BURNER ASSEMBLY MODULE

Rather than injecting the waste fuel as a liquid steam into the primary fuel flame, atomization of the waste is recommended for more efficient combustion. The problems to overcome for waste firing in a cement kiln are flame impingement on the inner wall of the kiln and pre-ignition of the primary fuel. The trajectory of the atomized waste spray pattern must be positioned so that cement production is not interrupted. Figure B-5 illustrates possible burner configurations which could succeed in introducing an atomized waste stream into the primary fuel flame. Because of heat radiation from the combustion zone of the kiln, a water- or air-cooled, jacketed gun assembly may be necessary to prevent the waste from pre-volatilizing inside the waste gun pipe.

B-5 BURNING ZONE TEMPERATURE MEASUREMENT

Gas temperature measurement in the combustion zone (highest temperature zone) has long been recognized as technically desirable for assurance that a sufficient destruction temperature has been achieved in an incineration system. This measurement, however, is difficult to make with accuracy. At cement kilns the burning zone temperature is typically monitored by measuring the flame temperature with optical pyrometry, and this was the case at San Juan Cement.

The optical pyrometer and radiation pyrometer are not designed to measure gas temperature, and should not be used for this purpose, as results may be extremely misleading. Excessive error is also encountered when gas temperatures about 540°C (1000°F) are measured with a bare thermocouple because of radiation effects [43].

The high-velocity and multiple-shield high-velocity thermocouples (HVT and MHVT), developed to correct for radiation effects, are the best instruments available for the measurement of high gas temperatures. Cross sections through single and MHVT thermocouples, developed to evaluate gas temperatures in the furnace and superheater sections for steam boiler testing, are shown in Figure B-6.

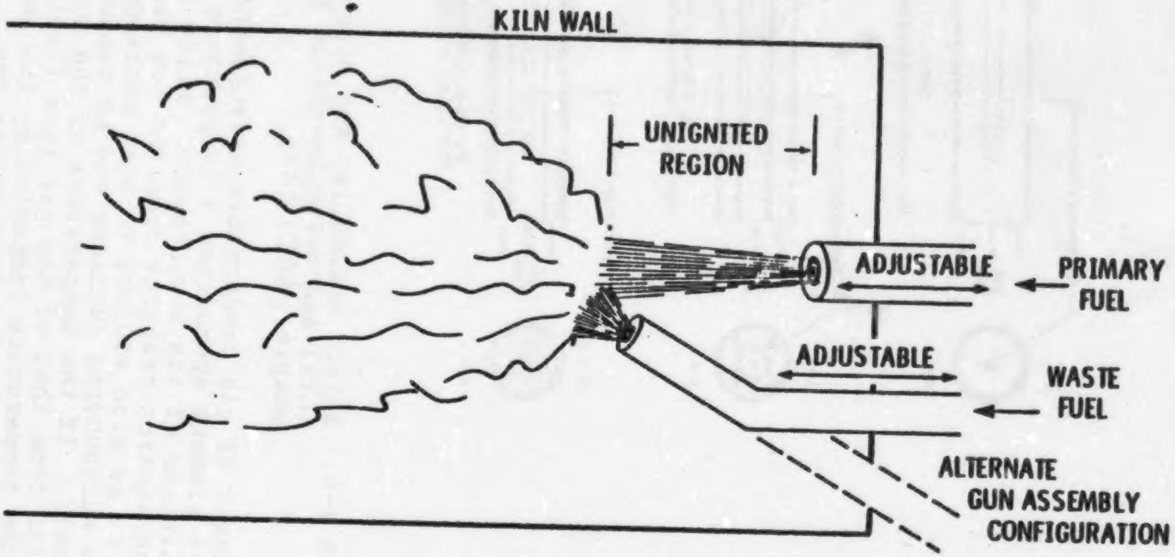
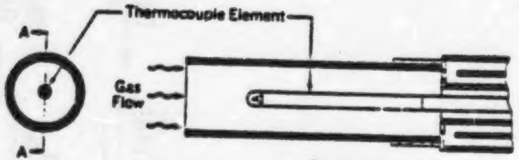
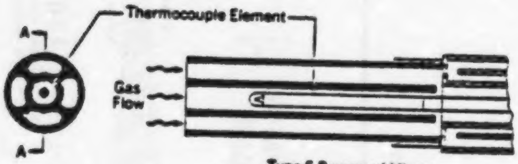

KILN WALL
UNIGNITED REGION
ADJUSTABLE
PRIMARY FUEL
ADJUSTABLE
WASTE FUEL
ALTERNATE GUN ASSEMBLY CONFIGURATION

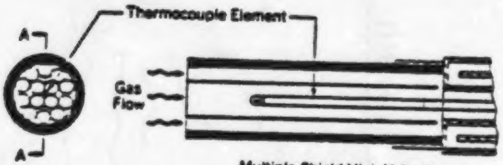
Figure B-5. Burner/nozzle configurations to allow for waste fuel atomization in a cement kiln.



Section A-A
High-Velocity-Thermocouple Shield Assembly



Type E Bureau of Mines
High-Velocity-Thermocouple Shield Assembly



Multiple-Shield High-Velocity-Thermocouple Shield Assembly

Figure B-6. Shield assemblies for high-velocity thermocouple (HVT) and multiple-shield high-velocity thermocouple (MHVT) [43].

In all cases of gas temperature measurement, the temperature-sensitive element approaches a temperature in equilibrium with the conditions of its environment. While it receives heat primarily by convection transfer from the hot gases in which it is immersed, it is also subject to heat exchange by radiation to and from the surrounding surfaces and by conduction through the instrument itself. If the temperature of the surrounding surfaces does not differ from that of the gas (gas flowing through an insulated duct), the temperature indicated by the instrument should accurately represent the temperature of the gas. If the temperature of the surrounding surfaces is higher or lower than that of the gas, the temperature indicated by the instrument will be correspondingly higher or lower than the temperature of the gas [43].

The amount of variation from the true temperature of the gas depends on the temperature and velocity of the gas, the temperature of the surroundings, the size of the temperature-measuring element, and the physical construction of the element and its supports. To correct for the errors in temperature caused by the surroundings in any particular installation, it is best to calibrate the instrument against a known and reliable determination of the gas temperature [43].

Since the transfer of heat by radiation is proportional to surface area, emmissivity, and the difference of the fourth powers of the absolute temperatures of source and receiver, it follows (the gases being considered as nominally transparent to the passage of radiant energy) that the effects of radiation increase as the temperature difference between the thermocouple hot junction and the surrounding surfaces increases. Also, since transfer of heat to the thermocouple by convection is proportional to a power of gas mass velocity and to the first power of the temperature difference between gas and thermocouple, it follows that the temperature of the junction may be brought more nearly to the true temperature of the gas by increasing the rate of mass velocity and convection heat transfer while shielding the junction from the influence of radiation [43].

The surfaces surrounding the location of a gas traverse in the cement are cooler than the gases (see Figure 2-4). Consequently, the readings from a bare unshielded thermocouple will indicate lower temperatures than those obtained with an HVT. For the same reason, an HVT will generally indicate lower values than an MHVT. If the gas traverse location is very near the kiln flame, however, the opposite radiation effect may apply.

Measurements with the MHVT closely approach true gas temperature. In the MHVT, the thermocouple junction is surrounded by multiple shields, all of which receive heat by convection induced by the high rate of gas flow. In this manner, the transfer of heat by radiation is so reduced that there is virtually no exchange of heat between the junction and the innermost shield. Because of the small flow areas which rapidly become clogged by ash, practical use of the MHVT is limited to clean gas conditions. Where traverses are taken in dust- or slag-ladden gases, it is usually necessary to use the HVT and correct the readings by comparison with the results from an MHVT obtained under clean-gas conditions [43].

For temperatures exceeding 1200°C (2200°F), noble-metal thermocouples are required. When platinum couples are used in gases ranging from 1425°C to 1650°C (2600-3000°F) or higher, appreciable calibration drift may occur even while taking measurements requiring only several minutes of exposure time [43].

It must be emphasized, however, that development of such a system capable of accurate measurement under cement kiln conditions with sufficient protection to keep kiln contents from breaking or otherwise compromising, will be a formidable undertaking.

B-6 MISCELLANEOUS CONCERNS

Several of the following concerns may have to be addressed in obtaining a permit for a permanent waste fuel burning facility.

Personnel Health and Safety

The health and safety of the public and of plant employees should be considered of major importance in any industrial installation design or operation. The effect of plant emissions on the plant employees is also a primary concern. Often, plant employees in direct contact with the industrial processes for extensive periods of time are in the greatest immediate danger. This section will not attempt to define the multitude of work-related hazards facing hazardous waste incinerator workers, but will concentrate on these areas of concern: equipment for worker protection and procedures for worker protection [44].

- Synthetic Gloves - These provide skin protection for the hand and arm, as required. Synthetic means rubber, polyethylene, or other impervious materials. Full-arm-length gauntlets or sleeve protectors can also be used.

- Synthetic Aprons - Materials specified for synthetic gloves also apply to aprons. Disposable-type coveralls or laboratory coats may be preferred for many tasks at an incinerator facility.

- Respiratory Protective Devices - There are three types of these devices: (1) air-purifying respirators, (2) supplied-air respirators, and (3) self-contained breathing apparatuses.

  The air-purifying respirators utilize an aerosol filter for protection against particulate matter and/or a chemical cartridge for protection against certain known gases of vapors. The choice of cartridge is dictated by the hazard involved.

  The supplied-air respirators are supplied with air remote from the hazardous location, usually through a breathing-air manifold and hoses. The self-contained breathing apparatus is normally used only in emergency situations. Use only devices that are certified by NIOSH.

- Adequate Ventilation - Ventilation in an area must be sufficient to prevent harmful exposure to toxic materials. The threshold-limit value (TLV) for an individual chemical vapor or type of dust refers to the time-weighed concentration for a normal workday, under which it is believed that nearly all workers may be repeatedly exposed, day after day, without harmful effect. If this value is exceeded, then a "ceiling" value applies. This ceiling value should not be exceeded (emergency situations such as spills require the use of protective equipment). Exposure to concentrations above the TLV up to the ceiling value are not desirable, but are permitted as long as the overall eight-hour time-weighted average (TWA) does not exceed the TLV.

If inadequate ventilation is indicated (TLV is exceeded) for any operation or area, immediate use of a personal air-supply system is engaged. A permanent solution involving good engineering practices is then desirable and should be implemented as soon as possible.

- Full Suit - This is a suit that provides head-to-toe protection for the hazard involved.

- Line Breaks - Line breaks include broken flanges on lines not previously exposed to the atmosphere, and drained and repacking of valves and pumps, where there exists a potential for hazardous streams in concentrated form or under pressure. In this type of operation, the following protective equipment is usually required: full-rubber acid-suit consisting of rubber coat, rubber pants, acid gloves, rubber boots under the pants, and rubber hood.

- Repairs - Repairs apply to work performed on equipment or lines that handled hazardous waste streams, which had previously been opened to the atmosphere, and which have been drained and proven to be under no pressure. Since the hazardous potential still exists, goggles or an approved hood and gloves are typically required. After flushing with water--or a neutralizer agent where feasible--and the danger potential no longer exists, as determined by supervision, hazardous-material protection is no longer required. If the underfoot area is still puddled or wet from flushing and draining, rubber overshoes are usually required.

  If a pump is not delivering, and troubleshooting or priming is necessary, goggles, gloves, and full face shields with coat or apron should be worn even though no breaks in the line have occurred.

Facility Housekeeping

Good housekeeping plays a key role in occupational health protection. Basically, it is another tool in addition to those other facility safeguards listed for preventing dispersion of dangerous contaminants. Housekeeping is always important; where there are toxic materials, it is paramount.

Immediate cleanup of any small spills of toxic material is a very important control measure. A regular cleanup schedule using vacuum cleaners or lines is the only truly effective method of removing liquids from a work area. Use of chemical sorbents may be used but these require that the liquid/sorbent mixture be removed, usually manually, to prevent personnel exposures during repair operations. An air hose for blowing away dust should never be used.

Accumulations of all types of dust should be cleaned at regular intervals from overhead pipes, beams, and machines, particularly from bearings and other heated surfaces. It must be understood that all organic as well as many inorganic materials, if ground finely enough, will burn and propagate flame. Roofs also are kept free from combustible refuse. Such cleaning perferably is done by vacuum removal, because blowing down with air may disperse dusts into dangerous clouds.

Maintenance

Testing is a prime activity in a maintenance program, particularly for a hazardous waste incineration facility. While alarm systems, spill-alert systems, and fail-safe devices are available, a testing program usually periodically creates situations which require fail-safe devices to demonstrate their operation. Other tasks such as visual and electronic inspections will make up the remainder of a maintenance program and are included on prepared forms. These forms should state the optimum timing for each inspection as well as the required frequency.

Incidences of excess emissions can be reduced by good operation and maintenance (O&M) practices and a comprehensive preventative maintenance program. With these practices, control equipment can provide maximum benefit.

Firefighting/Emergency Personnel and Equipment

In addition to automatic sprinkler and extinguisher equipment, the plant should have a written fire emergency plan of attack.

A fire emergency plan includes:

(1) An emergency squad composed of personnel from operations, maintenance, front office supervision, and guard force--specifically selected and trained in emergency control techniques and equipment.

(2) Emergency planning taking into account the plant's alarm system, communications, organization responsibilities, evacuation possibilites, available emergency equipment, mutual aid arrangements, and traffic control.

(3) Emergency crews engaged in continual training.

(4) Emergency squad members thoroughly trained in comprehensive first-aid treatment.

(5) Emergency squad members familiar with firefighting equipment.

(6) Emergency public evaluation since the incomplete combustion of hazardous wastes can release toxic substances. Complete combustion can release acid gases if the wastes contain halides or sulfur.

A manual containing the relevant information is prepared and distributed to those responsible for executing the plan. This is reviewed at least annually, and updated as needed.

Emergency crews must undergo continual training because the time available to respond to an actual emergency is usually quite limited. Furthermore, the infrequency of calls to action can, with time, erode the ability of crews to respond with the speed usually required. Crews are typically provided for all shifts and trained to handle all types of emergencies: fire, toxic-gas releases, chemical spills, serious injury, and personnel rescue.

Emergency-squad members are usually thoroughly trained in comprehensive first-aid treatment, including cardiopulmonary resuscitation, handling of breathing apparatus, and emergency rescue procedures; and are familiar with station and ambulance first-aid equipment. In addition, they learn the different types of fires, extinguishing agents, the proper protective clothing for firefighting, and become familiar with firefighting equipment, including hoses, nozzles, portable extinguishers, wheel units, fire trucks, and with the plant's fire-protection systems. Finally, field training in firefighting with protective clothing includes experience extinguishing "Christmas-tree," impingement, pan and spill, and other types of fires.

At a sprinklered property, the most important function of person nel assigned to the emergency organization is to assure at all times that the automatic sprinkler protection will operate as intended. At the start of the fire it must be made certain that sprinkler valves are open and fire pumps operating as needed; during the fire, that valves are not closed too soon; and after the fire, that opened sprinklers are replaced and protection restored promptly.

An emergency squad is designed to be capable of containing small fires, preventing them from developing into large, uncontrollable ones that can cause loss of life and property.

Stormwater Diversion

Stormwater drainage and other innocuous discharges should be segregated and handled within the battery limits of the industrial kiln facility. These streams are normally collected and directed by pipe, drainage ditches, or area grading through one outlet from the area to a local feeder ditch. The single outlet or outfall also contain a spill control structure and gate which can be closed to contain contaminated drainage that may occur due to leaks or spills in the facility area. Feeder ditches generally border the plant sites along roadways and eventually drain outside the plant.

Facility process areas should be paved and curbed or diked to contain leaks, spills, and washdowns, and these directed to a process sump area. The process sumps are pumped to the appropriate waste treatment facility.

Outlying facility storage tanks, pumps, and unloading facilities should be curbed, diked, or paved for leak and spill control to prevent contamination of area drainage. The contained areas are then drained and valved to allow normal storm water drainage. These valves, which are normally closed, are opened for storm water drainage. In the event a contamination occurs, it is contained for subsequent treatment and appropriate disposal.

Operations Plan

An operations plan includes the following:

(1) Classification of waste fuels to be handled and estimated quantities

(2) Methods and processes utilized

    (a) Facility capacity

    (b) Detailed description of each process

(3) Storage and disposal procedures

    (a) Plans for receipt, checking, processing, segregating incompatible wastes, and odor control

    (b) Life of facility based on projected use

(4) Monitoring Procedures

    (a) Monitoring of kiln operating parameters

    (b) Monitoring and recording of incoming waste fuels

(c) Leachate control and groundwater monitoring (optional)

(d) Security system

(e) System for monitoring water and air pollution affecting area outside the site

(f) Air pollution control device monitoring

(5) Administrative Procedures

(a) Hours of operation/day and days/week

(b) Security procedures including entry control, hours manned, lighting, and other procedures to prevent unauthorized entry

(c) Procedures planned and equipment available in case of breakdowns, inclement weather, or other abnormal conditions

(d) Description of recordkeeping procedures, types of records to be kept, and use of records by management to control the operation.

(e) List of general qualifications of key operating personnel

(f) Maintenance and inspection schedules

Operations Manual

Once in operation, the industrial kiln facility will maintain operation guides or manuals, covering the routine workings of the plant. An operations guide can include:

(1) A scaled engineering drawing, pictorial flow diagram, or scale model of the plant, showing all major components by name and function.

(2) A set of formal drawings at the plant for reference by operational and maintenance personnel

(3) Equipment manuals

(4) Equipment catalogs

(5) Spare parts lists

(6) Job or task functions for each assignment during a typical shift

Emergency Manual or Handbook

An emergency manual or handbook is prepared which specifies the plan-of-action for any type of emergency the facility may reasonably expect to encounter. These include weather extremes (severe cold, heavy snowfall, hail damage, hurricances, tornados, high winds, or lightning damage), floods, earthquakes, power outages, bomb scares, fires and explosion, and spills.

Leak Detection and Repair Plan

Any facility that processes hazardous air pollutants as described under Section 112 of the Clean Air Act must develop a Leak Detection and Repair Plan (LDRP) to aid in reducing fugitive emissions [4]. The LDRP must be certified by the owner of the facility as meeting the fugitive emission criteria established by the EPA under the Clean Air Act. The plan is to be reviewed and updated, as required, once every three years, or within 90 days of a major modification at the facility. At the minimum, the LDRP:

(1) Develops a schedule and recordkeeping program for routine surveillance and/or monitoring of fugitive emissions.

(2) Establishes a written plan for detection and repair of leaks, and a reasonable schedule for repair.

(3) Provides a written plan for sampling procedures, housekeeping (e.g., small spill cleanup) and onsite waste handling.

(4) Develops recordkeeping procedures for all aspects of the LDRP and saves these records for one year.

(5) Establishes a written plan for specifying sufficient personnel to fulfill the LDRP, and provides a training program with a written manual.

Hazardous Chemical Spill Handling Plan

Most plants' safety, disaster, or operating plans and manuals do not fulfill the requirement for a spill-handling plan. The key to adequate spill-handling is decisionmaking. None of the above manuals or procedures supply all the information required to make the decisions necessary to cope with the spill of a hazardous material. Thus, a chemical-spill-handling plan will fill an information need, but will not program decisions.

In a spill-handling plan, the decisions that must be made in a spill incident are defined. First, the plant or plant superintendent must accept the fact that a spill has occurred, based on information from his monitoring systems. The most immediate steps are those aimed at the protection of human life. If the information obtained about the location and nature of the leak/spill shows that the threat to life is "immediate and great," the decision should be to "shut down - all persons immediately take cover." Otherwise, the decision should be to "cleanup the area."

The "immediate cover" for persons is a spill response usually described by the plant disaster/emergency plan, whereas the protection of employees during the "cleanup the area" procedure is ordinarily contained in a safety plan. It is the lack of information between these two extremes that the spill-response plan fills.

Once a spill-response leader has been chosen, the decisionmaking process continues toward containment actions and disposition procedures. Figure B-7 diagrams the decisionmaking process and information needed in a spill-handling situation, as well as the requirements for improving the spill response.

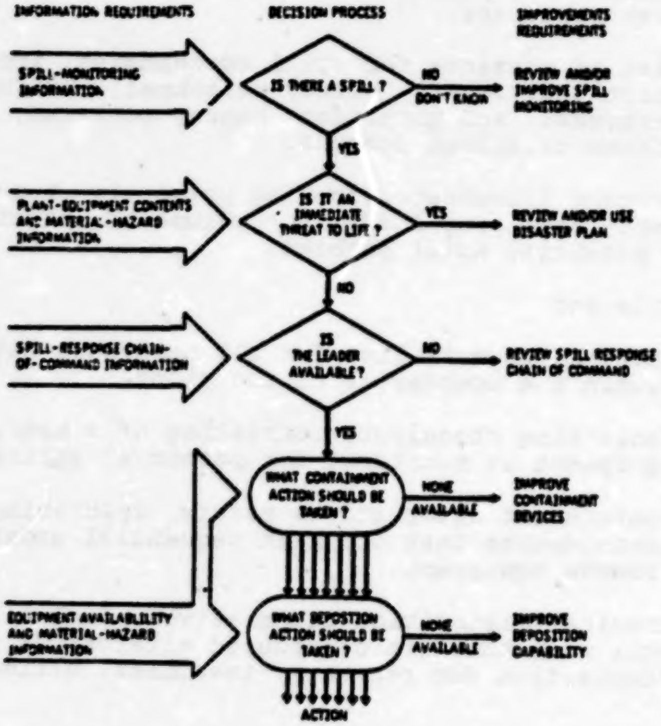

INFORMATION REQUIREMENTS
DECISION PROCESS
IMPROVEMENTS REQUIREMENTS
SPILL-MONITORING INFORMATION
IS THERE A SPILL ?
NO
DON'T KNOW
REVIEW AND/OR IMPROVE SPILL MONITORING
YES
PLANT-EQUIPMENT CONTENTS AND MATERIAL-HAZARD INFORMATION
IS IT AN IMMEDIATE THREAT TO LIFE ?
YES
REVIEW AND/OR USE DISASTER PLAN
NO
SPILL-RESPONSE CHAIN-OF-COMMAND INFORMATION
IS THE LEADER AVAILABLE ?
NO
REVIEW SPILL RESPONSE CHAIN OF COMMAND
YES
WHAT CONTAINMENT ACTION SHOULD BE TAKEN ?
NONE AVAILABLE
IMPROVE CONTAINMENT DEVICES
EQUIPMENT AVAILABILITY AND MATERIAL-HAZARD INFORMATION
WHAT DEPOSITION ACTION SHOULD BE TAKEN ?
NONE AVAILABLE
IMPROVE DEPOSITION CAPABILITY
ACTION

Figure B-7. Spill-response diagram illustrating the interrelating information available, decisions to be taken, and improvements needed [45].

A spill-handling plan is written as an easy-to-consult document for decisionmaking, and includes:

(1) Monitoring all possible spills of materials

(2) Identifying of all plant equipment and other contents it may have (can be separated into convenient process groupings or modules)

(3) Describing hazards of materials that would comprise potential spills.

(4) Designating the chain of command during a spill incident

(5) Specifying equipment available for containment, and disposition alternatives in response to a spill.

Every spill-handling plan has seven relatively independent parts that fulfill the five needs mentioned above. These parts are kept as autonomous as possible to facilitate the upgrading of each one. The seven parts are:

(1) List of contacts for spill emergencies, including plant/shift individuals, safety personnel, environmental control personnel, and government agency contacts, with home and office telephone numbers.

(2) Process flowsheets, showing primarily those pieces of equipment containing sufficient volume of material to constitute a potential spill problem.

(3) Site map.

(4) Chemical-effects list for all hazardous materials located within the boundaries of the plant.

(5) Monitoring checklist, consisting of a matrix indicating how equipment is monitored for potential spills.

(6) Containment alternatives matrix, describing the series of containments that occur in sequential order for various process equipment.

(7) Chemical-disposition alternatives, including a listing of equipment that are considered alternative places of material disposition for recovery, treatment, ultimate disposal.

Facility Security

Facility security is management's responsibility. Basic security problems are protection of property and controlling access to the facility. Security procedures for hazardous waste disposal facilities are described in the Federal Register, Vol. 45, No. 98, Part 265 - Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities, Subpart B - General Facility Standards, 265.14 Security, pg. 33235, May 19, 1980.

Operator Practices and Training

Operator practices and training of personnel ensure the smooth, efficient running of a hazardous waste incineration facility. Some of the areas covered under practice and training include:

(1) Selection of personnel, pre-employment physicals, periodic examinations

(2) Training; e.g., supervisory, operator, emergency

(3) Operating manual use; e.g., development of the manual, process description, material specifications, safety considerations

(4) Instruction of personnel

(5) Start-up and shut-down procedures; e.g., problems of start-up, normal shut-down, emergency shut-down

(6) Maintenance and inspection

(7) Preparation for emergencies; e.g., recognition, alarms, simulated emergencies, disaster drills

Operator training procedures and rules are described in the Federal Register, 265.16 - Personnel Training.

Loss Prevention Program

A loss prevention program embodies many of the facets of an emergency handbook, operations manual, and personnel training. Usually, loss prevention encompasses a whole facility concept and can include other concerns such as:

(1) Accident prevention
(2) Industrial Health and Hygiene
(3) Environmental Control
(4) Fires and explosions
(5) Fire prevention measures
(6) Explosion prevention measures

Laboratory for Waste Verification and/or Characterization

Analytical data should be made available for all waste fuels to be incinerated. The physical and chemical properties and the combustion characteristics of each chemical waste or general classification of wastes, shall be determined before incineration. Only after such analysis can successful waste disposal be carried out safely and without violation of air or water pollution regulations as set forth by state and federal agencies.

A minimal but complete laboratory facility requires a working area, including office facilities, of about 223 m^2 (2,400 sq ft). Provisions are made for air, water, gas, and electricity, preferably both AC and DC. The laboratory furniture includes benches, sinks, fume hood, shelving, glassware racks and a refrigerator. Good lighting and air-conditioning are also important. Identification of laboratory equipment needed for analyses of chemical wastes follows. Specific requirements depend on the types of wastes to be processed and type of incinerator used. If the equipment for sophisticated analytical methods is not available in-house, the analyses can be performed by commercial analytical laboratories.

(1) Typical laboratory equipment to determine physical properties:

- (a) Specific gravity balance - specific gravity of liquids.
- (b) Brookfield viscosimeter - viscosity measurement of liquids and sludges.
- (c) Imhoff cones and centrifuge with graduated tubes - measurement of percent solids by volume.
- (d) Sieving machine for screen analysis (to 100 micron) and HIAC particle counter (100-5 micron) - particle size measurement (optional).
- (e) Cleveland open cup flash point tester - flash and fire point determinations.
- (f) Oven and balances - percent solids and moisture by weight.
- (g) Gas chromatograph-mass spectrometry and infrared apparatus to identify organic substances which may be toxic (optional).
- (h) Differential thermal analyzer - explosion characteristics and fusion temperature (optional).
- (i) Juno meter or equivalent - sensitive to alpha, beta and gamma rays for radioactivity (optional).

(j) Bomb calorimeter to determine waste fuel heating value.

(k) Karl Fisher apparatus to determine moisture content of hazardous waste.

(2) Laboratory equipment to determine chemical properties.

(a) Gas chromatograph with flame ionization detector and/or electron capture defector (GC/FID and GC/ EC) to confirm that the chemical composition of the waste fuel is similar to the shipping manifest.

(b) Standards of waste fuel's chemical components for laboratory quality assurance/quality control.

(c) Muffle furnace, oven, balances - for percent ash by weight.

(d) Orsat, fyrite techniques for flue gas analyses to provide data for excess air calculations.

(e) pH meter and automatic titrator - acidity and alkalinity measurement.

(f) Emission spectrograph for concentration and presence of metals (optional).

(g) Atomic absorption spectrometer for concentration of metals and elements (optional).

(3) Laboratory equipment to determine combustion properties:

(a) Calorimeter (previously listed) for heating value and combustibility.

(b) Orsat (previously listed) for CO_2, CO, O_2, and N_2 analysis.

(c) Flue gas analyzer (previously listed) for analysis at various excess air rates.

(d) Mass spectrometer (previously listed) for hazardous products of combustion (optional).

B-7 OPERATION PROCEDURES

During the demonstration burn program, operation procedures for use by the kiln operators were developed with assistance of the plant shift supervisor. Procedures developed for use at San Juan Cement are presented below (bilingually).

NORMAL OPERATION

A - A flow of ___ gallons per minute shall be maintained.

B - At the % indicator, read ___% and at the recorder read ___.

C - At the gallons counter the flow can be verified by using the chronometer in the same way it is used at the Floco meter to check fuel oil flow.

IN CASE OF KILN SHUT-DOWN

A - If kiln stops - close inlet to kiln valve.

B - Place solenoid switch in "Off" position (emergency shut-off valve).

C - Open air valve in order to clean pipe and nozzle.

D - Once the system is clean - close air valve - close inlet to kiln valve - disconnect "hose" from the pipe by loosening joint at inlet of pipe.

E - Stop the pump.

F - Remove pipe.

G - Note: Regulating valve should never be closed completely in order to avoid damaging valve seat.

NOTES TO PLANT FOREMEN

A - Plant foreman must inspect frequently the area around both tanks as well as the length of the pipe to the kiln in order to detect any spillage or leak of synthetic fuel.

B - In case of a synthetic fuel leak system shall be stopped and tank discharge valves shall be closed.

RE-STARTING OPERATION

A - Once kiln reaches normal operating conditions - start pump #1 (amber light at control room board).

B - Place pipe into position inside blast pipe and connect hose to pipe.

C - Making sure that air valve is closed, open inlet to kiln valve.

D - Place solenoid switch in "On" position.

E - Open inlet to manifold valve.

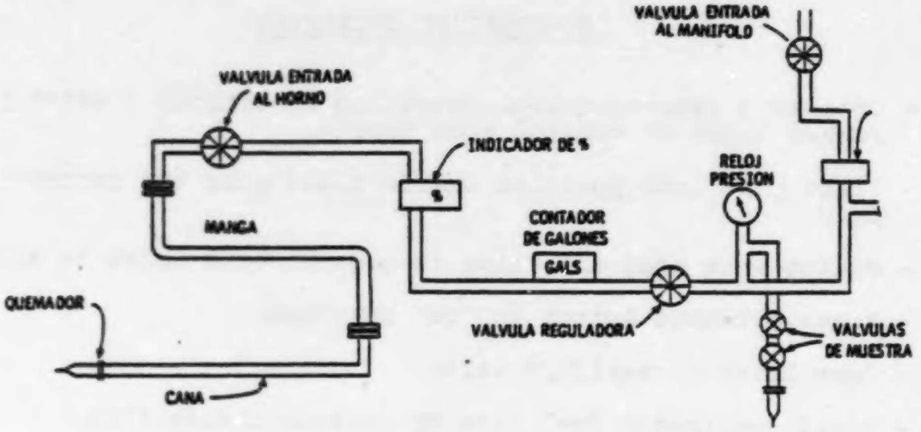
F - Verify synthetic fuel flow by looking inside kiln.

G - Verify quantity of synthetic fuel flow by observing % indicator which should read _____%.

H - If flow is not correct - adjust by means of regulating valve.

I - Adjust oxygen % in the kiln to what it was before starting of synthetic fuel burning.

J - Adjust fuel oil flow according to conditions of kiln at burning zone, chains, baghouse, etc.


VALVULA ENTRADA AL MANIFOLD
VALVULA ENTRADA AL HORNO
INDICADOR DE %
%
RELOJ PRESION
MANGA
CONTADOR DE GALONES
GALS
QUEMADOR
VALVULA REGULADORA
VALVULAS DE MUESTRA
CANA

OPERACION NORMAL

A - Se mantendra un fluid de_______ gals por minuto.

B - En el indicador de % se mostrada como _____% y en la grafica se leera como _____.

C - En el contrador de galones se puede verificar el flujo usando el cronometro segun se usa con el Floco para el petroleo.

EN CASO DE PARADA

A - Si se para el horno - se cerre la valvula de entrada

B - Se pone el switch del solenoid en "Off".

C - Se abre valvula de aire para limpiar tuberia y mechero.

D - Una vez que el sistema esta limpio - cierre el aire - cierre valvula entrada al horno - desconecte manga de la caña desenroscando tulerca de la manga.

E - Pare la bomba.

F - Remueva la caña.

G - Valvula reguladora no debe ser cerrada en ningun momento para evitar su obstruccion.

MEMORANDUM DEL PLANT FOREMAN

A - El Plant Foreman debera inspeccionar con mucha frecuencia tanto el area de los tanques del sintetico como todo el trayecto de la tuberia para asi detectar custquier fuga del liquido.

APPENDIX C

B - En caso de fuga del sintetico se parara el sistema y se cerraran las valvulas de salida del tanque immediatamente.

HYDROGEN CHLORIDE ACID SAMPLING AND ANLYSIS METHOD

REANUDACION DE OPERACION

A - Una vez este el horno este en condiciones normales prenda bomba del sintetico #1 (Ambar)

B - Posicione caña en el mechero y conecte manga a la caña.

C - Abra valvula de entrada al horno. Asegurese que valvula de aire este cerrada.

D - Ponga switch del solenoid en "On".

E - Abra valvula de entrada.

F - Verifique el flujo del sintetico a traves de la ventanilla.

G - Verifique cantidad de sintetico en el indicador del sintetico que debero leer ___%.

H - De no ser asi - adjuste lo con valvula reguladora.

I - Adjuste % de oxigeno en el horno a lo que estaba antes de comenzar el sintetico.

J - Adjuste el flujo de petroleo segun condiciones del horno en zona de fuego, cadenas, baghouse, etc.

APPENDIX C

HYDROGEN CHLORIDE SAMPLING AND ANALYSIS METHOD

INTERIM METHOD - DETERMINATION OF HYDROGEN CHLORIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The hydrogen chloride is trapped in a dilute solution of sodium acetate, forming ionic sodium chloride. The sample is analyzed using a chloride ion specific electrode and an expanded scale millivolt/pH meter. Note: The sampling and analysis procedure is basically a modification of the NIOSH S246 procedure for hydrogen chloride in air and the standard procedure for SO_2 determination (EPA Reference Method 6); the HCl method utilizes the same sampling equipment as EPA Method 6 (i.e., probe, glassware, pump, dry gas meter, etc.) and the same reagents and operating range of NIOSH Procedure S246.

1.2 Applicability. This method is applicable for the determination of hydrogen chloride emissions from stationary sources. The NIOSH method has been validated over the range of 3.5 - 14 mg HCl/m^3 (2.5 - 10 ppm) at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 15 L sample. The probable useful range of this method is 1-20 mg HCl/m^3 for 15 L samples. The upper limit of the range of the method is dependent on the capacity of the midget bubbler (first impinger). If higher concentrations than those tested are to be sampled, smaller sample volumes should be used, or, alternatively, an additional impinger containing sodium acetate solution can be placed in the impinger train. The collection efficiency for hydrogen chloride, in the NIOSH method, was determined to be 0.981, standard deviation of 0.005 (essentially 1.00), when sampled for 15 minutes at 0.94 Lpm from a test atmosphere containing 70 mg/m^3 (50 ppm). Therefore, no correction for collection efficiency is necessary.

1.3 Interferences. This method is not specific for hydrogen chloride since any chloride ion which is trapped in the sodium acetate solution will be measured and give a positive interference.

Sulfide ion must be absent because it poisons the chloride ion specific electrode. Touch a drop of the sample to a piece of lead acetate paper to check for sulfide ion. If sulfide is present, it is removed by addition of a small amount of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck a drop of the sample with lead acetate paper. Avoid a large excess of cadmium carbonate and long contact time with the solution. Filter the sample through a small plug of glass wool and proceed with the analysis.

Other common interfering ions are bromide ion, iodide ion, and cyanide ion. For interference free operation, the chloride ion level must be at least 3×10^2 times the bromide ion level, 2×10^6 the iodide ion level, and 5×10^6 the cyanide ion level.

Sufficiently high concentrations of species which form extremely stable complexes with silver ion (such as ammonia and thiosulfate) will also interfere and will result in reading higher chloride ion activity than actually exists (positive interference). For less than a 1% error, the maximum ratio of ammonia to chloride concentration should be 0.12 and the maximum ratio of thiosulfate ion to chloride ion concentration should be 0.01.

1.4 Precision and Accuracy. The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 3.5 - 14 mg/m^3 was 0.064. This value corresponds to a standard deviation of 0.45 mg/m^3 at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 2.

A collection efficiency of 0.981 was determined for the collecting medium. On the average, the concentrations obtained using the overall sampling and analytical method were 2.7% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final calculation result in Section 6.3.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 1, and component parts are discussed below. The HCl method utilizes the same sampling equipment used in EPA Reference Method 6. A heated glass-lined probe is used with the temperature maintained at 300°F or at stack temperature, whichever is greater. A pyrex wool plug is inserted in the inlet end of the probe in the same manner as required by Method 6. The impinger train, which is immersed in an ice bath during sampling, consists of one midget bubbler and three midget impingers connected by glass U tubes and clamps. Bubbler No. 1 and impinger No. 2 should contain 10 mL of the absorbing solution (0.5 M NaOAc). Impinger No. 3 should contain 15 mL of 3% H_2O_2 solution, which will remove SO_2 from the sample stream. Impinger No. 4 is a dry impinger which functions to remove moisture from the sample stream. The impinger train is interfaced with the probe by using a short, right angle bend glass adapter with the appropriate standard taper ground glass joints at either end. A drying tube is inserted between the impinger train and the pump to further dry the gas sample and protect the pump and meter. A standard Method 6 control box with umbilical cord is used to complete the sample train. A sampling rate of 0.5 to 1.0 Lpm for 15-30 minutes is recommended with a total sample volume of 15 L per sample.

2.1.1 Probe. Borosilicate glass, approximately 6 mm inside diameter, with a heating system to prevent water condensation and filter to remove particulate matter. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers. One midget bubbler, with medium-course glass frit, and three 30 mL midget impingers. The bubbler and midget impingers must be connected in series with

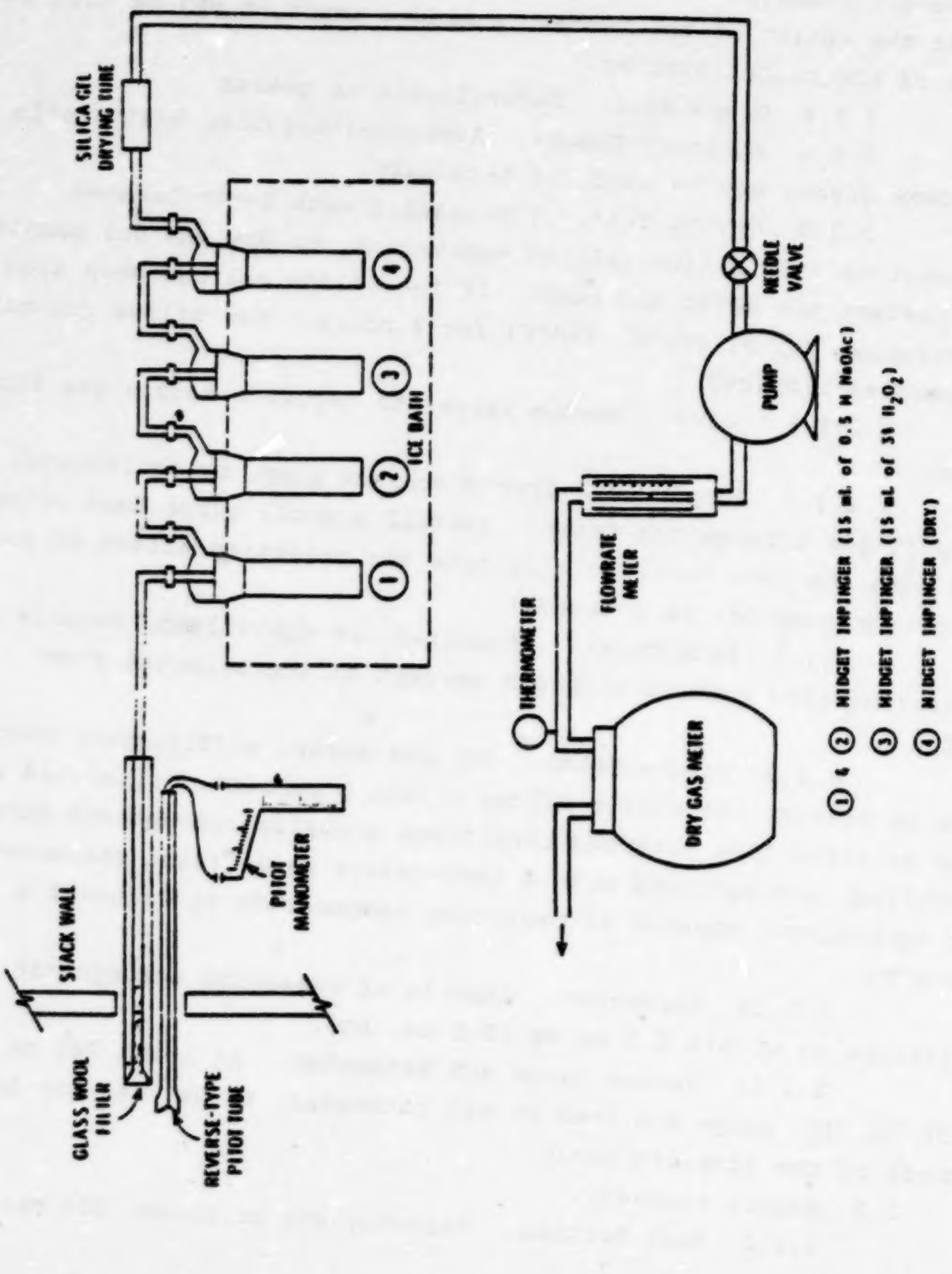

STACK WALL
GLASS WOOL FILTER
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
1
2
3
4
ICE BATH
SILICA GEL DRYING TUBE
NEEDLE VALVE
PUMP
FLOWRATE METER
THERMOMETER
DRY GAS METER
① & ② MIDGET IMPINGER (15 mL of 0.5 N NaOAc)
③ MIDGET IMPINGER (15 mL of 3% H_2O_2)
④ MIDGET IMPINGER (DRY)

Figure D-1. HCl sampling train.

leak-free connectors. Silicone grease may be used, if necessary, to prevent leakage.

At the option of the tester, a midget impinger may be used in place of the midget bubbler.

2.1.3 Glass Wool. Borosilicate or quartz.

2.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

2.1.5 Drying Tube. Tube packed with 6- to 16-mesh desiccating type silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

2.1.6 Valve. Needle valve, to regulate sample gas flow rate.

2.1.7 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate.

2.1.9 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 3°C (5.4°F).

2.1.10 Barometer. Capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

2.1.11 Vacuum Gauge and Rotameter. At least 760 mm Hg (30 in. Hg) gauge and 0-40 cc/min rotameter, to be used for leak check of the sampling train.

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500 mL.

2.2.2 Storage Bottles. Polyethylene, 100 mL, to store impinger samples (one per sample).

2.3 Analysis.

2.3.1 Pipettes. Volumetric type, 1 mL, 2 mL,3 mL, 5 mL, and 10 mL sizes.

2.3.2 Volumetric Flasks. 100 mL size, five, and 1,000 mL size, one.

2.3.3 Orion Model 94-17A chloride ion specific electrode, or equivalent.

2.3.4 Reference Electrode. Orion 90-02 double junction, or equivalent.

2.3.5 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.

2.3.6 Beakers. Polyethylene, 50 mL capacity.

2.3.7 Magnetic stirrer and stirring bars for 50 mL beakers.

2.3.8 Polyethylene Containers. Used to store diluted sodium chloride standards, 100 mL.

3. Reagents

All chemicals must be ACS reagent grade or equivalent.

3.1 Sampling

3.1.1 Collection Medium: 0.5 M sodium acetate solution. Dissolve 82 g of sodium acetate in doubly distilled water and dilute to 2 L.

3.1.2 Doubly distilled water.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (V/V) with deionized, distilled water (15 mL is needed per sample). Prepare fresh daily.

3.2 Sample Recovery.

3.2.1 Collection Medium. Used to rinse impingers and glassware.

3.2.2 Doubly distilled water. Used to rinse the peroxide-containing impinger.

3.3 Analysis.

3.3.1 Water. Doubly distilled, as in 3.1.2.

3.3.2 Sodium Chloride. For preparation of standards.

3.3.3 Standard Chloride Solutions.

3.3.3.1 Dissolve 0.584 g of sodium chloride in doubly distilled water and dilute to 1 L for 10^{-2} M (Cl^-) or 354 µg Cl^-/mL. Adjust the pH to 5 with glacial acetic acid. This solution is stable for about two months. The following more dilute standards should be prepared fresh weekly and kept in polyethylene containers.

3.3.3.2 Dilute 10 mL of 10^{-2} M (Cl^-) to 100 mL with 0.5 M sodium acetate for 10^{-3} M (Cl^-) or 35.4 µg/Cl^-/mL.

3.3.3.3 Dilute 5 mL of 10^{-2} M (Cl^-) to 100 mL with 0.5 M sodium acetate for 5 x 10^{-4} M (Cl^-) or 17.7 µg Cl^-/mL.

3.3.3.4 Dilute 3 mL of 10^{-2} M (Cl^-) to 100 mL with 0.5 M sodium acetate for 3 x 10^{-4} M (Cl^-) or 10.6 µg Cl^-/mL.

3.3.3.5 Dilute 2 mL of 10^{-2} M (Cl^-) to 100 mL with 0.5 M sodium acetate for 2 x 10^{-4} M (Cl^-) or 7.1 µg Cl^-/mL.

3.3.3.6 Dilute 1 mL of 10^{-2} M (Cl^-) to 100 mL with 0.5 M sodium acetate for 10^{-4} M (Cl^-) or 3.5 µg Cl^-/mL.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train. Measure 10 mL of 0.5 M sodium acetate into the midget bubbler and another 10 mL into a midget impinger. Measure 15 mL of 3 percent hydrogen peroxide into a midget impinger. Leave the final midget impinger dry. Assemble the train as shown in Figure 1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-Check Procedure. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak check procedure is identical to that used in EPA Reference Method 6.

4.1.3 Sample collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate between 0.5 and 1.0 liter/min (1-2 CFH) as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run (15 liters total sample). Take readings (dry gas meter, temperatures at dry gas meter and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gas leaving the last impinger at 20°C (68°F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak check as in Section 4.1.2. If a leak is found, void the test run.

4.2 Sample Recovery. Disconnect the impinger, measure and record on the data sheet the volume of water collected, and pour the contents of the first two impingers into a polyethylene bottle for shipment. Rinse the impingers and impinger stems with 5 mL of collection medium, adding the rinse to the polyethylene sample bottle. Mark the fluid level. Seal and identify the sample container. Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

Discard the contents of impingers Nos. 3 and 4, and rinse with distilled water.

A "blank" sample of collection medium should be handled in the same manner as the impingers containing samples (fill, seal, and transport) except that no air is sampled through this blank sample.

4.3 Sample Analysis. Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, void the sample.

The sample in each polyethylene container is analyzed separately.

Transfer the contents of each polyethylene container to a 50 mL polyethylene beaker which has been pre-marked at 25 mL. Rinse the polyethylene container with 2-3 mL of distilled water and add rinse to the beaker. Adjust the pH to 5 with acetic acid. Dilute each sample to 25 mL with distilled water and stir the samples with a magnetic stirrer. If the sample size is greater than 25 mL, then dilution factor corrections must be made for comparison with the chloride ion standards.

Lower the chloride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

5. Calibration

5.1 Metering System. Same as EPA Reference Method 6.

5.2 Analytical Standards and Calibration. Prepare a series of chloride standard solutions in the pre-marked 50 mL beakers diluting 10 mL of each of the chloride standards prepared in Section 3.3.3 to a volume of 25 mL with doubly distilled water, starting with the most dilute standard. Place the chloride ion electrode and the reference electrode in the stirred solution. Record the resultant millivolt readings to the nearest 0.5 millivolt.

Plot the millivolt readings vs. the chloride ion concentrations of the standards on semi-log paper. The chloride ion concentration in µg/25 mL is plotted on the logarithmic axis.

6. Calculations

6.1 Sample Content. Read the weight in µg corresponding to each millivolt reading from the standard curve. No volume corrections are needed because the standard curve is based on µg/25 mL volume, and the volume of the samples is identical to the volume of the standards.

Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

Calculate the μg of hydrogen chloride by multiplying the μg chloride ion found by 1.028, which is the conversion factor to convert μg chloride ion to μg hydrogen chloride.

6.2 Dry gas sample volume, corrected to standard conditions.

$$V_{m(std)} = K_1 Y \frac{V_m P_{bar}}{T_m}$$

where $V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in. Hg for English units.

Y = Dry gas meter calibration factor.

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

T_m = Average dry gas meter absolute temperature, °K (°R).

6.3 Concentration in Stack Gas. The concentration of the analyte in air sampled can be expressed in mg/m³ (mg/m³ = μg/liter).

$$C_{HCl} = \frac{\mu g \text{ (Section 6.1)}}{V_{m(std)} \text{ (Section 6.2)}} \times \frac{mg}{1{,}000\ \mu g}$$

Another method of expressing concentration is ppm.

$$ppm = mg/m^3 \times \frac{24.04}{MW} \times \frac{760}{P} \times \frac{T + 273}{293}$$

where P = pressure of air sampled, mm Hg.

T = temperature of air sampled, °C.

24.04 = molar volume at 20°C and 760 mm Hg, liter/mole.

MW = molecular weight of analyte, g/mole.

760 = standard pressure, mm Hg.

293 = standard temperature, °K.

7. Bibliography

1. NIOSH Method S246, NIOSH Manual of Analytical Methods, Second Edition, Volume 3, U.S. Department of Health, Education, and Welfare, Cincinnati, OH. DHEW (NIOSH) Publication No. 77-157-C. April 1977.

2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

3. Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources. 40 CFR 60, 41782-41784. August 18, 1977.